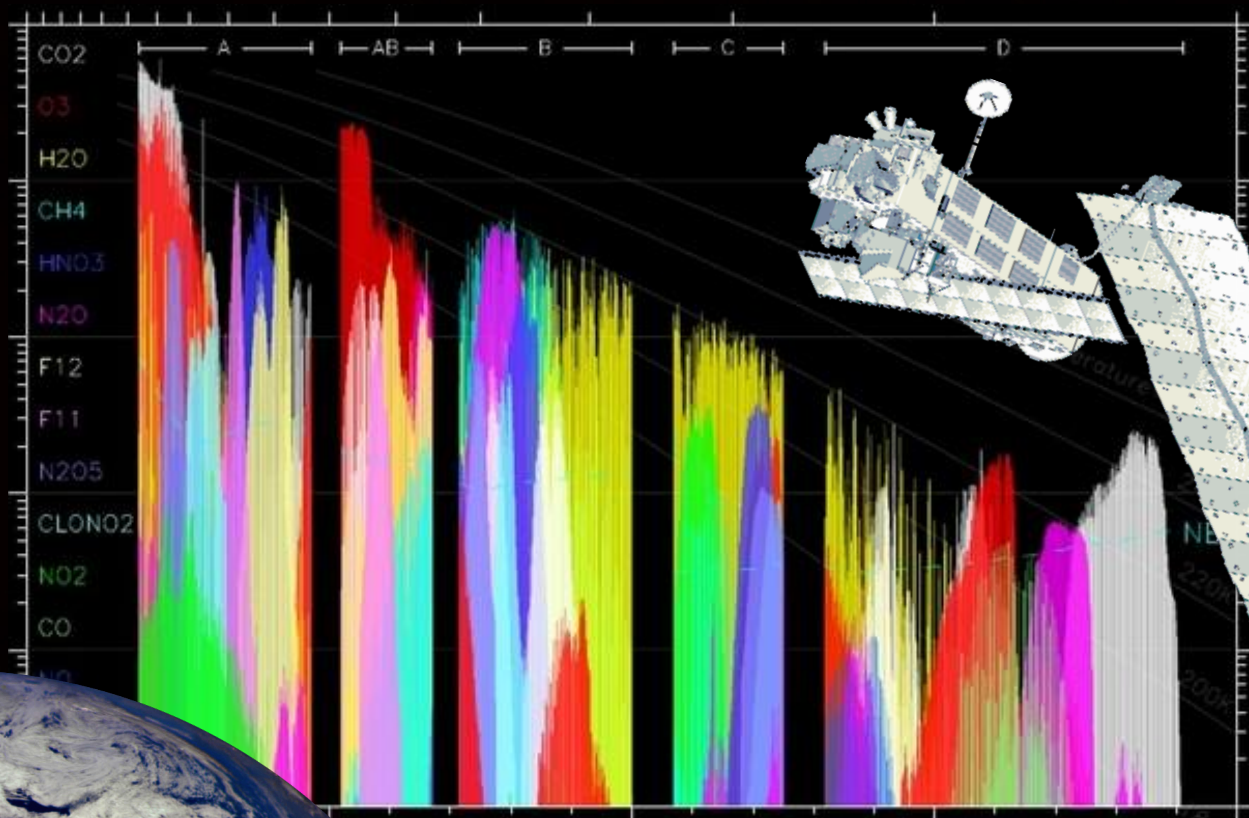


# RETRIEVAL OF CO<sub>2</sub> AND COLLISIONAL PARAMETERS FROM THE MIPAS SPECTRA IN THE EARTH ATMOSPHERE

TESIS DOCTORAL REALIZADA POR:

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INSTITUTO DE ASTROFÍSICA DE ANDALUCÍA  
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# Inversión del $\text{CO}_2$ y de parámetros colisionales de los espectros de MIPAS en la atmósfera terrestre

Ángel Aythami Jurado Navarro

## Memoria de Tesis

presentada para optar al grado de  
Doctor en Ciencias Físicas por la Universidad de Granada

Dirigida por:

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Granada, a 19 de octubre de 2015



*A mi mujer y a mi hijo.*





*Examina tus sentimientos, sabes que es verdad.*  
DARTH VADER (EPISODIO V)

*Yo he visto cosas que vosotros no creeráis.  
Atacar naves en llamas más allá de Orión.  
He visto Rayos-C brillar en la oscuridad cerca de la puerta de Tannhäuser.  
Todos esos momentos se perderán en el tiempo... como lágrimas en la lluvia.  
Es hora de morir.*  
ROY BATTY (BLADE RUNNER)

... Para ir audazmente donde ningún hombre ha ido antes  
CAPITÁN JAMES T. KIRK (STAR TREK TOS INTRO)



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X

Antonio Jurado Torres y Alicia Navarro Alonso y a mi hermano y amigo, Tony.



# Resumen

El CO<sub>2</sub> es un gas de efecto invernadero importante y es una de las piezas fundamentales en el balance energético de la atmósfera terrestre Tierra y, en consecuencia, en su estructura térmica. Su emisión en 15  $\mu\text{m}$  representa el mecanismo más importante de enfriamiento de la estratosfera, mesosfera y baja termosfera. La absorción de la luz del sol en las bandas del CO<sub>2</sub> cercanas al infrarrojo (2.7 y 4.3  $\mu\text{m}$ ) contribuyen significativamente al calentamiento atmosférico. Las transiciones ro-vibracionales de la molécula implicadas en estos procesos están en no equilibrio termodinámico local (no-ETL) en la media y alta atmósfera.

Desde el siglo pasado hasta el presente, se han realizado un gran número de estudios que muestran cómo la concentración del CO<sub>2</sub> está aumentando continuamente. El impacto de este incremento en el enfriamiento y el calentamiento de las distintas capas atmosféricas es evidente. Por ejemplo, la tendencia de la temperatura en la troposfera ha sido positiva mientras, en la mesosfera, ha sido negativa. Desde el principio de la industrialización, la humanidad ha ido emitiendo cada vez más cantidad de sustancias volátiles a la atmósfera cambiando su composición pero, todavía no tenemos respuestas claras sobre cuáles son sus efectos sobre los distintos cambios atmosféricos observados. Desde las primeras medidas de cohetes *in situ* en los setenta hasta las más recientes medidas de satélites de ocultación solar como ACE, o instrumentos de emisión en limbo como SABER, hemos aumentado considerablemente nuestro conocimiento sobre la abundancia del CO<sub>2</sub>. Todos estos estudios indican que un conocimiento más preciso de la distribución espacio-temporal del CO<sub>2</sub> en la mesosfera y la termosfera es crucial para conocer mejor el balance energético de esta región, de su dinámica (que acopla ésta con las regiones inferiores), y la respuesta de la atmósfera a los cambios antropogénicos.

Vale la pena mencionar la gran dificultad de analizar las emisiones de las distintas bandas del CO<sub>2</sub> en el infrarrojo y de invertir su abundancia a partir de las medidas de dichas emisiones (principalmente provenientes de los complejos procesos del no-ETL). El conocimiento preciso de las poblaciones en no-ETL de los estados del CO<sub>2</sub> que emiten cerca de 4.3  $\mu\text{m}$  ha limitado la precisión de las abundancias del CO<sub>2</sub> derivadas de medidas de emisión en limbo. Los espectros de MIPAS, con su resolución espectral sin precedentes, nos permiten conocer mucho mejor los distintos procesos de no-ETL del CO<sub>2</sub> y, por lo tanto, mejorar la inversión del CO<sub>2</sub> a partir de medidas de emisión tomadas en 4.3  $\mu\text{m}$ .

Así, el **principal objetivo** de este trabajo es invertir las distribuciones globales

de la abundancia del CO<sub>2</sub> (razón de mezcla en volumen o vmr) a partir de los espectros infrarrojos de alta resolución de MIPAS en la mesosfera y termosfera con alta precisión. Esto requiere primero invertir los principales parámetros colisionales de no-ETL (incluyendo su dependencia con la temperatura) que afectan a las poblaciones de los niveles del CO<sub>2</sub> a partir de espectros de MIPAS en las regiones de 4.3 y 10  $\mu\text{m}$ , lo que constituye el **segundo objetivo principal** de esta tesis. Dado que estos parámetros se necesitan en la inversión del CO<sub>2</sub>, este objetivo se realizará en primer lugar y, después, invertimos la concentración relativa (razón de mezcla) del CO<sub>2</sub>. Una vez que las abundancias del CO<sub>2</sub> están invertidas, analizamos la calidad de los datos y realizamos un minucioso análisis de errores, tanto de los parámetros colisionales como de las concentraciones de CO<sub>2</sub>. Además, realizamos un estudio de validación comparando los datos del CO<sub>2</sub> de MIPAS con medidas independientes previas de ACE y SABER. Por otra parte, también analizamos las principales características de las distribuciones globales de CO<sub>2</sub> obtenidas en base a los procesos químicos y dinámicos reinantes en la alta atmósfera con la ayuda del modelo 3D 'Whole Atmosphere Community Climate Model' (WACCM).

En lo concerniente a la inversión de los principales parámetros colisionales, hemos desarrollado un esquema de inversión en no-ETL y lo hemos aplicado a los espectros de MIPAS en 10 y 4.3  $\mu\text{m}$ . Los extensos intervalos, tanto en altura como en latitud, han permitido también obtener la dependencia con la temperatura de los parámetros colisionales en el rango de 130 a 250 K. Todos los parámetros se han invertido con una precisión mucho mejor que la obtenida hasta ahora. Los resultados más notables son:

- El  $k_{vv,2}$  derivado aquí tiene una dependencia con la temperatura mayor que la utilizada hasta ahora, y es considerablemente mayor que valores previos por debajo de 300 K, abarcando factores entre 1 y 1.5 desde 300 K a 130 K. Este resultado es de suma importancia debido a que este parámetro controla las poblaciones de los niveles del CO<sub>2</sub> (10011) y (10012), y por consiguiente también controla la radiación atmosférica cerca de 4.3 y 2.7  $\mu\text{m}$  de la alta mesosfera y baja termosfera.
- Los parámetros colisionales que controlan la transferencia V-V de niveles de alta energía,  $k_{vv,3}$  y  $k_{vv,4}$ , han sido invertidos por primera vez. Hemos invertido una dependencia con la temperatura de  $1/T^{0.6}$ , un poco más fuerte que  $1/\sqrt{T}$ , con valores mayores que parámetros previos cerca en un 20% a temperaturas mesosféricas. No hemos encontrado diferencias significativas entre  $k_{vv,3}$  y  $k_{vv,4}$ .
- Hemos invertido valores de  $k_{F1}$  y  $k_{F2}$  muy distintos a los utilizados anteriormente.  $k_{F1}$  es de 5 a 43 veces menor que lo usado hasta ahora. El rango de error de  $k_{F2}$  es considerablemente menor que los valores usados hasta ahora, que diferían en más de un factor 10. Esto conduce a cambios considerables en la radiación atmosférica de las dos principales bandas calientes que emiten en 4.3  $\mu\text{m}$ , disminuyendo su contribución en un 20-30% para condiciones de latitudes medias.
- El parámetro colisional  $k_{vt}$  derivado es un factor 0.4–0.7 menor que los utilizados

anteriormente. El parámetro colisional  $k_{O(^1D)}$  derivado junto con  $k_{vt}$ , es muy similar a los valores publicados en la literatura reciente.

- Los nuevos parámetros tienen efectos muy importantes en las radiancias atmosféricas en las regiones espectrales de 10, 4.3 y 2.7  $\mu\text{m}$  cuando se comparan con las obtenidos usando los parámetros colisionales típicos utilizados en trabajos previos. Su efecto es principalmente notorio en medidas efectuadas en el limbo (geometría tangencial), aunque también importante en medidas en nadir.

Hemos invertido las concentraciones del  $\text{CO}_2$  a partir de los espectros de emisión de MIPAS en la región de 4.3  $\mu\text{m}$  obtenidos en su modo de observación de alta atmósfera (UA) en condiciones diurnas (versión de los datos  $\text{CO}_2\_620.0$ ). El  $\text{CO}_2$  invertido cubre desde los 70 km hasta los 140 km. La inversión se ha realizado utilizando un esquema de inversión para no-ETL desarrollado en IAA/IMK. Esta inversión del  $\text{CO}_2$  tiene la ventaja de usar otras medidas simultáneas de parámetros atmosféricos proporcionadas por MIPAS, como la temperatura cinética (hasta los  $\sim 100$  km) de la región del  $\text{CO}_2$  de 15  $\mu\text{m}$ , la temperatura termosférica del NO en 5.3  $\mu\text{m}$ , las medidas de  $\text{O}_3$  (hasta  $\sim 100$  km, que permiten una fuerte restricción en la concentración de  $\text{O}(^1D)$  por debajo de  $\sim 100$  km), y un cálculo preciso del  $\text{O}(^1D)$  por encima de  $\sim 100$  km. El modelo de no-ETL incorpora los parámetros colisionales vibración-vibración y vibración-traslación derivados de los espectros de MIPAS antes descritos.

La precisión de los perfiles de vmr del  $\text{CO}_2$  varían con la altura abarcando desde un  $\sim 1\%$  por debajo de 90 km, hasta un 5% sobre los 120 km, siendo mayor que el 10% por encima de los 130 km. Los valores mayores a alturas más elevadas se deben a la menor relación señal/ruido del instrumento. La precisión varía muy poco con la latitud y la estación, con pequeños cambios debidos a las condiciones de iluminación solar.

Los perfiles de  $\text{CO}_2$  invertidos tienen una resolución vertical de unos 5–7 km debajo de 120 km, con un incremento de hasta 12 km en  $\sim 100$  km, y entre 10 y 30 km en 120–140 km.

Las características más importantes observadas en el  $\text{CO}_2$  invertido se pueden resumir en:

- El  $\text{CO}_2$  invertido muestra las características principales que se esperan y predicen por los modelos: la abrupta caída del vmr del  $\text{CO}_2$  por encima de 80–90 km, causada por la predominancia de la difusión molecular, y el cambio estacional de la distribución latitudinal. Esta última se ve reflejada en mayores abundancias de  $\text{CO}_2$  en el verano polar entre 70 km y  $\sim 95$  km, y menores en el invierno polar, ambas inducidas por las ramas ascendentes y descendentes de la circulación meridional, respectivamente. Por encima de  $\sim 95$  km, el  $\text{CO}_2$  es más abundante en el invierno polar que en latitudes medias y que en el verano polar, debido a la inversión de la circulación meridional en esa región.
- Las distribuciones latitudinales típicas del solsticio y equinoccio se encuentran en los datos muy frecuentemente, durante casi 2.5 meses en cada estación, y la

transición solsticio/equinoccio ocurre generalmente de manera rápida, tardando alrededor de un mes.

- Hemos encontrado un pequeño descenso en el vmr del CO<sub>2</sub> de MIPAS alrededor de los 80 km en el invierno polar. No estamos seguros de si es real, debido, por ejemplo, a un CO<sub>2</sub> remanente de la estación previa, o si se debe a un comportamiento inadecuado del esquema de inversión causado por una combinación de la elevada iluminación solar y las bajas temperaturas de la mesopausa polar.

Con el objetivo de validar el vmr del CO<sub>2</sub> de MIPAS, hemos realizado una comparación detallada con las medidas más recientes tomadas por los instrumentos ACE y SABER a bordo de satélites. Los resultados principales se pueden resumir en:

- En equinoccio, MIPAS muestra un buen acuerdo general con ACE. Las medidas del CO<sub>2</sub> de MIPAS son un poco mayores que las de ACE a 80-100 km. A mayores altitudes, las diferencias varían con la latitud, estando siempre dentro de un  $\pm 20\%$ .
- En equinoccio, el acuerdo de MIPAS con SABER es incluso mejor que con ACE, estando dentro de un 5% por debajo de 100 km. En la región de 100-120 km, MIPAS tiende a ser un  $\sim 20\%$  mayor en regiones polares y un  $\sim 10-20\%$  menor cerca de los trópicos.
- Durante el solsticio hay, en general, un muy buen acuerdo entre las medidas del CO<sub>2</sub> de los tres instrumentos. El acuerdo entre MIPAS y ACE es similar al de condiciones de equinoccio, pero hay una clara distinción en el verano polar, donde la caída del vmr del CO<sub>2</sub> con la altitud por encima de  $\sim 100$  km es más pronunciada en MIPAS que en ACE. Este comportamiento está también presente en los datos de SABER (en un acuerdo excelente con MIPAS) y es incluso más prominente (probablemente demasiado pronunciado) en las simulaciones de WACCM (ver debajo).
- El acuerdo de MIPAS con SABER es, en general, muy bueno. El CO<sub>2</sub> de MIPAS es, sin embargo, menor (un  $\sim 5\%$ , y probablemente demasiado bajo) sobre los 80 km en el verano polar. Por otro lado, SABER parece ser demasiado bajo en 60–80 km en el invierno polar en enero, y demasiado alto en 65-95 km en el invierno polar en febrero.
- WACCM sobreestima generalmente el CO<sub>2</sub> de los tres instrumentos por encima de  $\sim 90$  km en latitudes medias y en los trópicos durante el equinoccio. Aún así, lo contrario ocurre en el solsticio en latitudes medias y altas para el hemisferio de verano, cuando el CO<sub>2</sub> de WACCM disminuye más pronunciadamente que el CO<sub>2</sub> de los tres instrumentos a dichas altitudes.

Con objeto de obtener conclusiones a escala global también hemos comparado los promedios zonales y perfiles en bandas latitudinales para el promedio **anual** de 2010. Los resultados muestran que:



- Las medidas de MIPAS son generalmente mayores (un  $\sim 5\%$ ) que las de ACE a 80-100 km y un 20-30% menores a 100-120 km.
- MIPAS y SABER concuerdan muy bien hasta los 100 km. En 100-120 km, también concuerdan bien cuando se promedia sobre todas latitudes, pero MIPAS es generalmente mayor que SABER excepto cerca del ecuador, donde MIPAS es menor. Esto es, en la región de 100-120 km y globalmente, el  $\text{CO}_2$  de ACE es el mayor, SABER el menor y el de MIPAS está entre ambos.
- Las medidas de  $\text{CO}_2$  de SABER entre 100 y 120 km son globalmente menores que los valores de MIPAS, ACE y WACCM.

De la comparación detallada del  $\text{CO}_2$  de MIPAS con las simulaciones de WACCM extraemos las siguientes conclusiones:

- En términos generales WACCM reproduce los principales patrones de la distribución vertical del  $\text{CO}_2$  y las variaciones estacionales y latitudinales observadas en los datos de MIPAS.
- Por debajo de aproximadamente 100 km la concordancia es muy buena, con diferencias menores que  $\pm 10\%$  (para  $P_r = 2$ ) excepto para las condiciones de solsticio cerca de 90-100 km, donde pueden llegar hasta el 20%, siendo WACCM menor. En el polo de verano, cerca de 80 km, MIPAS es menor hasta un 5%, que podría señalar un problema en la inversión del  $\text{CO}_2$  de MIPAS.
- A alturas de 100-140 km, el  $\text{CO}_2$  de WACCM es generalmente mayor que el de MIPAS en equinoccio y a casi todas las latitudes con diferencias de 20-100%. En los hemisferios de verano, sin embargo, el  $\text{CO}_2$  de WACCM es generalmente menor en 20-70%. En los hemisferios de invierno, el  $\text{CO}_2$  de WACCM es también generalmente mayor que MIPAS aunque no tan grande como en equinoccio.
- In general, MIPAS sugiere un valor del número de Prandtl bajo,  $P_r = 2$ , esto es, una mayor difusión turbulenta, sobre todo por debajo de los 100 km. En la región de 100 a 120 km, sin embargo, las simulaciones de WACCM con  $P_r=4$  contrarrestan las sobre-estimaciones de WACCM con  $P_r=2$  y arrojan, globalmente, un mejor acuerdo con MIPAS.
- Las diferencias entre las distribuciones del  $\text{CO}_2$  de MIPAS y WACCM nos plantean nuevas cuestiones aún por resolver. Así, por ejemplo, ¿pueden las distintas distribuciones latitudinales/estacionales del  $\text{CO}_2$  de MIPAS/WACCM ser debidas a una variación latitudinal/estacional de la difusión turbulenta?; ¿es la circulación residual de la baja termosfera demasiado fuerte en WACCM?; ¿se deben dichas diferencias a una subestimación en WACCM de las pérdidas fotoquímicas del  $\text{CO}_2$ ?

Finalmente, la concentración del  $\text{CO}_2$  de MIPAS promediada entre  $60^\circ\text{S}$  y  $60^\circ\text{N}$  muestra por encima de  $\sim 100$  km una disminución de 2010 a 2011, que es consistente con la mayor actividad solar en 2011. Este resultado es también consistente con las

medidas de SABER y las predicciones de WACCM. Las medidas de ACE muestran una disminución entre 95 y 110 km pero no entre 110 y 120 km.

En un futuro cercano, el trabajo más urgente sería completar la inversión del CO<sub>2</sub> para todo el periodo de medidas de MIPAS en el modo de atmósfera alta (UA): desde el 2005 hasta el final de la misión Envisat en 2012. Esta base de datos del CO<sub>2</sub> cubriría casi un ciclo solar completo y, por lo tanto, podría ser utilizado para estudiar la tendencia del CO<sub>2</sub>. De particular importancia es comprobar si el CO<sub>2</sub> muestra una tendencia en la media y alta atmósfera mayor que la esperada del aumento antropogénico del CO<sub>2</sub> en la baja termosfera, como se ha observado recientemente en las medidas de ACE y SABER.

MIPAS tiene la ventaja de proveer simultáneamente y globalmente, además del CO<sub>2</sub>, la abundancia del CO, y cubrir mayores alturas (hasta 140 km) que otros instrumentos anteriores. Este hecho permite estudiar en detalle la química del CO<sub>x</sub> (CO y CO<sub>2</sub>) y la dinámica de la termosfera media, una región prácticamente inexplorada.

Otro trabajo potencial de gran interés para llevarse a cabo en el futuro es el estudio del enfriamiento infrarrojo de la alta atmósfera. La comparación de las tasas de enfriamiento del CO<sub>2</sub> y del NO calculadas con datos de MIPAS y aquellas medidas por SABER serían de mucho valor. También, la comparación con simulaciones de WACCM serían de mucha utilidad, ya que MIPAS ofrece importantes restricciones con las medidas de la temperatura y las concentraciones (razón de mezcla) del CO, CO<sub>2</sub> y NO.

En la parte de desarrollo de algoritmos, sería muy útil adaptar este esquema de inversión para las inversiones del CO<sub>2</sub> a partir de los modos de observación de MIPAS de media atmósfera (MA, 20–100 km) y de 'noctilucent cloud' (NLC, 42-100 km).

# Abstract

CO<sub>2</sub> is an important greenhouse gas and is one of the master pieces in the energy balance of the Earth and, therefore, in its thermal structure. Its 15  $\mu\text{m}$  emission represents the most important cooling mechanism of the stratosphere, mesosphere and lower thermosphere. Absorption of sunlight in the near-infrared CO<sub>2</sub> bands (2.7 and 4.3  $\mu\text{m}$ ) contribute significantly to the atmospheric heating. The involved ro-vibrational transitions of the molecule are in a non local thermodynamic equilibrium (non-LTE) in the middle and upper atmosphere.

There are a large number of studies performed from the last century to the present day, showing how the CO<sub>2</sub> concentration is being continually increased. The impact of this increase in the cooling and heating of the different atmospheric layers is clear. For instance, the trend of the temperature in the troposphere has been positive meanwhile, in the mesosphere, has been negative. Since the beginning of industrialization, mankind has been emitting increasing amounts of harmful volatile substances into the atmosphere changing its composition but, we still have to answer what are the effects of these emissions on the different observed atmospheric changes. From the first *in situ* rocket measurements in the seventies until the most recent satellite measurements from solar occultation instruments like ACE or limb emission instruments like SABER, we have significantly gained knowledge about the CO<sub>2</sub> abundance. All these studies indicate that a more precise knowledge of the spatial-temporal distribution of CO<sub>2</sub> in the mesosphere and thermosphere is crucial for a better understanding of the energy balance of this important region, of its dynamical coupling to the regions below, and for understanding its response to anthropogenic changes.

It is worth to mention the great difficulty of analyzing the infrared emissions from the different CO<sub>2</sub> bands and to derive its abundance from these emissions, primary coming from the complex non-LTE processes. The accurate knowledge of the non-LTE populations of the CO<sub>2</sub> states emitting near 4.3  $\mu\text{m}$  has limited the accuracy of the CO<sub>2</sub> abundances derived from limb emission measurements. The MIPAS spectra, with its unprecedented high spectral resolution, allow to make significant advances in the knowledge of the different CO<sub>2</sub> non-LTE processes and hence, to improve the CO<sub>2</sub> retrieval from the emission measurements taken at 4.3  $\mu\text{m}$ .

Thus, **the major aim of this work** is to retrieve global distributions of the CO<sub>2</sub> abundance (volume mixing ratio or vmr) from the MIPAS high resolution infrared spectra in the mesosphere and thermosphere with high accuracy. This requires first to retrieve the main non-LTE parameters (including their temperature dependence)

affecting the population of the CO<sub>2</sub> levels from the MIPAS spectra in the 4.3 and 10  $\mu\text{m}$  regions, and constitutes the **second major objective** of this thesis. Because the collisional rates are required in the inversion of the non-LTE model, this objective is tackled first and later we perform the retrieval of the CO<sub>2</sub> vmr. Once the CO<sub>2</sub> abundances are retrieved, we analyze the quality of the data and perform a thorough error analysis. In addition, we perform a validation study by comparing the MIPAS CO<sub>2</sub> data with the previous independent measurements of ACE and SABER. Furthermore the main physical features of the retrieved global distribution of CO<sub>2</sub> are analyzed with the help of the 3D Whole Atmosphere Community Climate Model (WACCM).

Regarding the retrieval of the main collisional parameters, a non-LTE retrieval scheme, used in the previous analysis of the MIPAS non-LTE emission, has been applied to the MIPAS 10 and 4.3  $\mu\text{m}$  spectra. The wide altitude and latitude ranges have allowed to retrieve also the temperature dependence of the rates in the range of 130 to 250 K. All of them were retrieved with a much better accuracy that known before. The most salient results are:

- The  $k_{vv,2}$  derived here has a stronger temperature dependence than that used before. Also, it is significantly larger than previous values at temperatures below 300 K, ranging from a factor of 1 to 1.5 from 300 K to 130 K. This is a result of major importance since this rate controls the populations of the CO<sub>2</sub>(10011) and (10012) levels, and therefore the atmospheric radiation near 4.3  $\mu\text{m}$  and 2.7  $\mu\text{m}$  at upper mesospheric and lower thermospheric limb paths.
- The collisional rates for the V-V transfer from high energy levels,  $k_{vv,3}$  and  $k_{vv,4}$ , have been retrieved here for the first time. We have retrieved a temperature dependence of  $1/T^{0.6}$ , slightly stronger than  $1/\sqrt{T}$ , with values larger than previous rates by about 20% at mesospheric temperatures. We have not found any significant difference between  $k_{vv,3}$  and  $k_{vv,4}$ .
- We have retrieved values for the  $k_{F1}$  and  $k_{F2}$  rates very different from those previously used.  $k_{F1}$  is about 5 to 43 times smaller than reported before. The results for  $k_{F2}$  narrow significantly the uncertainty of previous estimates which show a spread of more than a magnitude. This leads to significant changes in the modeled atmospheric radiation of the two stronger 4.3  $\mu\text{m}$  second hot bands, decreasing them by 20-30% for mid-latitude conditions.
- The derived  $k_{vt}$  collisional rate is smaller (factor of 0.4 – 0.7) than the values used before. The  $k_{O(^1D)}$  collisional rate derived here jointly with  $k_{vt}$ , is very similar to the values published in recent literature.
- The new rates have very important effects on the atmospheric limb spectral radiances in the 10, 4.3 and 2.7  $\mu\text{m}$  spectral regions when compared to typical collisional rates used in previous works.

The CO<sub>2</sub> vmrs have been retrieved using MIPAS daytime limb emission spectra from the 4.3  $\mu\text{m}$  region in its upper atmosphere (UA) mode (data version CO2\_-620.0). The retrieved CO<sub>2</sub> covers from 70 km up to about 140 km. The inversion



has been performed by using a non-LTE retrieval scheme developed at IAA/IMK. It takes the advantage of other (simultaneous) MIPAS measurements of atmospheric parameters, as the kinetic temperature (up to  $\sim 100$  km) from the  $\text{CO}_2$   $15 \mu\text{m}$  region, the thermospheric temperature from the  $\text{NO}$   $5.3 \mu\text{m}$ , the  $\text{O}_3$  measurements (up to  $\sim 100$  km), which allows a strong constrain of the  $\text{O}(^1D)$  concentration below  $\sim 100$  km, and an accurate calculation of  $\text{O}(^1D)$  above  $\sim 100$  km. The non-LTE model incorporates the accurate vibrational-vibrational and vibrational-translational collisional rates derived from the MIPAS spectra and described above.

The accuracy of the retrieved  $\text{CO}_2$  vmr profiles varies with altitude ranging from  $\sim 1\%$  below 90 km, to 5% around 120 km and larger than 10% above 130 km. The larger values at higher altitudes are due to the lower signal-to-noise ratio. There are very little latitudinal and seasonal variations, which are driven by the solar illumination conditions.

The retrieved  $\text{CO}_2$  profiles have a vertical resolution of about 5–7 km below 120 km, with an increase of up to 12 km at  $\sim 100$  km, and between 10 and 20 km at 120–140 km.

The most important features observed on the retrieved  $\text{CO}_2$  can be summarized in:

- The retrieved  $\text{CO}_2$  shows the major general features expected and predicted by models: the abrupt decline of the  $\text{CO}_2$  vmr above 80–90 km, caused by the predominance of the molecular diffusion, and the seasonal change of the latitudinal distribution. The latter is reflected by higher  $\text{CO}_2$  abundances in polar summer from 70 km up to  $\sim 95$  km, and lower  $\text{CO}_2$  vmr in the polar winter, both induced by the ascending and descending branches of the meridional circulation, respectively. Above  $\sim 95$  km,  $\text{CO}_2$  is more abundant in the polar winter than at mid-latitudes and polar summer regions, caused by the reversal of the meridional circulation in that altitude region.
- The typical solstice and equinox latitudinal distributions are found in the data periods of about 2.5 months in each hemisphere, and the solstice/equinox seasonal transition usually takes place rather quickly, in about one month.
- We have found a small decrease in MIPAS  $\text{CO}_2$  vmr at  $\sim 80$  km at polar summer latitudes. We are not sure if this is real, e.g., remnant  $\text{CO}_2$  air from previous season, or a retrieval artifact caused by a combination of high solar zenith angles and low temperatures.

With the aim of validating the retrieved MIPAS  $\text{CO}_2$  vmr, a detailed comparison has been performed with the most recent satellite measurements taken by ACE and SABER. The major results can be summarized in:

- In equinox, MIPAS shows an overall good agreement with ACE. MIPAS  $\text{CO}_2$  measurements are slightly larger than those of ACE at 80–100 km. At higher altitudes, the differences varies with latitude, being comprised always within  $\pm 20\%$ .

- Also in equinox, the agreement of MIPAS with SABER is even better than with ACE, being within 5% below 100 km. In the 100-120 km region, MIPAS tends to be a ~20% larger in polar regions and a ~10-20% smaller near the tropics.
- During solstice there is, in general, a very good agreement between the CO<sub>2</sub> measurements of the three instruments. The agreement of MIPAS with ACE is similar as for equinox conditions, but there is a clear distinction in the polar summer, where the decay of the CO<sub>2</sub> vmr with altitude above ~100 km is steeper in MIPAS than in ACE. This behavior is also present in SABER data (in excellent agreement with MIPAS) and is it is even more prominent (probably too steep) in WACCM simulations (see below).
- The agreement of MIPAS with SABER is in general very good. MIPAS CO<sub>2</sub> is, however, smaller (~5%, and probably too low) around 80 km in the polar summer. SABER, on the other hand, seems to be too low at 60–80 km in the polar winter in January, and too high at 65-95 km in the polar winter in February.
- WACCM generally overestimates the CO<sub>2</sub> of the three instruments above ~90 km at mid- and tropical latitudes during equinox. However, the opposite occurs during solstice at mid and high latitudes of the summer hemisphere, when WACCM CO<sub>2</sub> decreases more pronouncedly than the CO<sub>2</sub> of the three instruments at those altitudes.

In order to draw more general conclusions we have also compared zonal mean cross-section and latitudinal band profiles for the annual mean of 2010. The results showed that:

- MIPAS measurements are generally larger (~5%) than ACE ones at 80-100 km and 20-30% smaller at 100-120 km.
- MIPAS and SABER agree very well up to 100 km. At 100-120 km, they also agree very well when averaging over all latitudes, but MIPAS is generally larger than SABER except near the equator where MIPAS is lower. That is, in the 100-120 km region, globally, ACE is the largest, SABER the smallest and MIPAS is in between.
- SABER CO<sub>2</sub> measurements between 100 and 120 km are globally smaller than MIPAS, ACE and WACCM.

From the detailed comparison of WACCM simulations with MIPAS observations we draw the following conclusions:

- Overall, WACCM reproduces the major CO<sub>2</sub> vertical distribution patterns and the seasonal and latitudinal variations observed in MIPAS data.

- Below about 100 km the agreement is very good, with differences smaller than  $\pm 10\%$  (for  $P_r = 2$ ) except for solstice conditions near 90-100 km where they can be as large as 20%, being WACCM smaller. In the polar summer, near 80 km, MIPAS is smaller by up to 5%, which might point to a problem in the MIPAS CO<sub>2</sub> retrieval.
- At 100-140 km altitudes, WACCM CO<sub>2</sub> is generally larger than MIPAS at equinox at almost all latitudes with differences of 20-100%. In the summer hemispheres, however, WACCM CO<sub>2</sub> is generally lower in 20-70%. In the winter hemispheres WACCM CO<sub>2</sub> is also generally larger than MIPAS although not as large as in equinox.
- In general, MIPAS favors more a value of  $P_r = 2$  (larger eddy diffusion), principally below around 100 km. In the 100-120 km region and above, however, WACCM simulations with  $P_r=4$  somehow mitigates the WACCM  $P_r=2$  overestimations and give an overall better agreement with MIPAS.
- The WACCM/MIPAS comparison give rise to new questions. For example, can the different MIPAS/WACCM CO<sub>2</sub> seasonal/latitudinal distributions be explained by a seasonal/latitudinal dependence of the eddy diffusion?; or is the lower thermosphere residual circulation in WACCM too strong?; or are they caused by an underestimation of the photochemical losses of CO<sub>2</sub> in WACCM?

Finally, the MIPAS global (60°S–60°N) CO<sub>2</sub> vmr above  $\sim 100$  km showed a decrease in 2011 with respect to 2010, which is consistent with the larger solar activity of 2011. This result is also consistent with SABER measurements and WACCM predictions. ACE measurements show also a decrease from 95 km up to 110 km but not between 110 and 120 km.

In a near future, the most urgent work will be to complete the CO<sub>2</sub> retrieval from the whole MIPAS optimized resolution upper atmosphere (UA) mode data set, from 2005 to the end of the Envisat mission in 2012. This CO<sub>2</sub> database will then cover nearly a complete solar cycle and, therefore, could be used to perform an inter-annual variability study. Of particular importance is to check if it shows also a trend of CO<sub>2</sub> in the middle and upper atmosphere larger than that expected from the CO<sub>2</sub> anthropogenic increase in the lower thermosphere, as has been recently reported from the ACE and SABER measurements.

The MIPAS CO<sub>2</sub> measurements have the advantages of providing simultaneously and globally, besides CO<sub>2</sub>, the CO abundance, and covering higher altitudes, up to 140 km. These would allow to study in detail the CO<sub>x</sub> chemistry and the dynamics of the middle thermosphere, practically an unexplored region.

Other potential work to be carried out in the future is the study of the upper atmosphere infrared cooling. Comparison of the CO<sub>2</sub> and NO cooling rates calculated with the MIPAS products and those measured by SABER would be very valuable. Also, comparison with WACCM simulations would be very useful, since MIPAS offers important constraints as the temperature, and the CO, CO<sub>2</sub> and NO relative concentrations.

On the algorithm development side, it would be very useful to develop the "setups" for the retrievals of CO<sub>2</sub> from the middle atmosphere (MA) and Noctilucent Cloud (NLC) MIPAS observations modes.

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# Chapter 1

## Introduction

### *Abstract*

The purpose of this chapter is to give an overview of the basic facts about the Earth's atmosphere and the role played by CO<sub>2</sub>. We begin presenting a glimpse of the history of the atmosphere and the effects of the CO<sub>2</sub> concentration in the evolution of global temperature along the 20<sup>th</sup> century. Next we highlight the scientific interest in the atmosphere and the different sounding techniques. Following that we describe the basic features of the Earth's atmosphere: its vertical structure, composition and the energy balance. Regarding CO<sub>2</sub>, first we give a general description of its spectra and energy levels. In the same section we explain the role of CO<sub>2</sub> in the cooling and heating of the mesosphere and lower thermosphere. Later we look back in order to summarize the CO<sub>2</sub> measurements taken during the last 40 years. Finally, we describe the motivation and objectives of this thesis.

### 1.1. Scope of this Work

The human being had lived without being aware of its impact on the Earth environment. This fact have become more evident with the development of industrial activities and the exponential growth of the population. Thus, we are now considering how human actions have gradually become the main driver of global environmental change<sup>1</sup>. Since the beginning of industrialization, mankind has been emitting increasing amounts of harmful volatile substances into the atmosphere changing its composition but we still have to answer what are the effects of these emissions on the different observed atmospheric changes.

Carbon dioxide, CO<sub>2</sub>, one of the master pieces in this jigsaw, is a well known greenhouse gas<sup>2</sup>. There are also other greenhouse gases in the atmosphere like H<sub>2</sub>O (water vapour) or CH<sub>4</sub> (methane). They warms the atmosphere by absorbing infrared emission critically affecting its energy balance. Thus the thermal structure and the atmospheric dynamics are shaped by them. The increasing release of this kind of

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<sup>1</sup>Steffen et al. (2015) classifies the climate change as a planetary boundary of increasing risk for the Earth System.

<sup>2</sup>Those gases with infrared activity that warms the atmosphere contributing to the greenhouse effect.

gases along 20<sup>th</sup> century is considered as one of the most important reasons of global warming (IPCC report, 2014). The Keeling curve, based on continuous measurements taken at the Mauna Loa Observatory in Hawaii, shows an increase in atmospheric CO<sub>2</sub> of ~25% since 1958 (Figure 1.1a). NOAA report (2015) shows the increment on the temperature of the oceans and the surface in the last 130 years (Figure 1.1b). On the other hand, in the middle and upper atmosphere, the radiative effects of greenhouse gases generate a cooling effect (Rishbeth and Roble, 1992; Akmaev, 2002). Focusing on temperature trends at these altitudes, Beig et al. (2003) analysed data from several studies in the 50 to 100 km region. In the lower and middle mesosphere a negative trend of 2-3 K per decade was found. A slightly larger cooling trend appears at low and mid-latitudes. In summary, there are several studies that shows how the increase of greenhouse gases, as CO<sub>2</sub>, changes the terrestrial thermal structure.

## 1.2. Earth's atmosphere basics

### 1.2.1. History

Let us start giving a brief review of the history of the Earth's atmosphere. It was originated about 4500 millions years ago from the outgassing of volcanism, principally hydrogen, water vapour, carbon dioxide and sulphur dioxide. About 4000 million years ago, the cooling of the planet led to the condensation of water vapour causing the origin of the oceans. Meanwhile the photodissociation of water molecules by solar UV radiation gave rise to hydrogen and oxygen. But the oxygen did not begin to rise significantly until about 3000 million years ago caused by photosynthesis of the first biological activities. This fact provoked a simultaneous decrease in CO<sub>2</sub> and, over a period of millions of years, the creation of the ozone layer. About 1500 million years ago the oxygen level in the atmosphere was stabilized and the atmosphere, roughly acquired the chemical composition of present day. Approximately, it is composed by 78% of N<sub>2</sub>, 21% of O<sub>2</sub> and 1% of minor gases like CO<sub>2</sub>, H<sub>2</sub>O, O<sub>3</sub>, CH<sub>4</sub>, and Ar. The gravitational attraction concentrates about half of the whole atmospheric mass in the first 5.5 km. The 99% of its mass is located within the first 15 km.

The atmosphere is also being affected by natural phenomena like the 11 years solar activity cycle. The amount of radiation and energetic particles reaching the upper atmosphere are continuously changing. This upper region is heated and expanded at solar maximum and cooled and compressed at the solar minimum. In addition, changes of the solar wind and its interaction with the magnetosphere impact the state of the upper atmosphere.

### 1.2.2. Vertical Structure

Along the 20<sup>th</sup> century different classifications of vertical layers of the atmosphere were proposed attending to different phenomena and/or concepts. The first were based on studies of the atmospheric conductivity by analyzing charged particles, the electrons and ions. Using this criterium we find a non-conducting atmosphere called



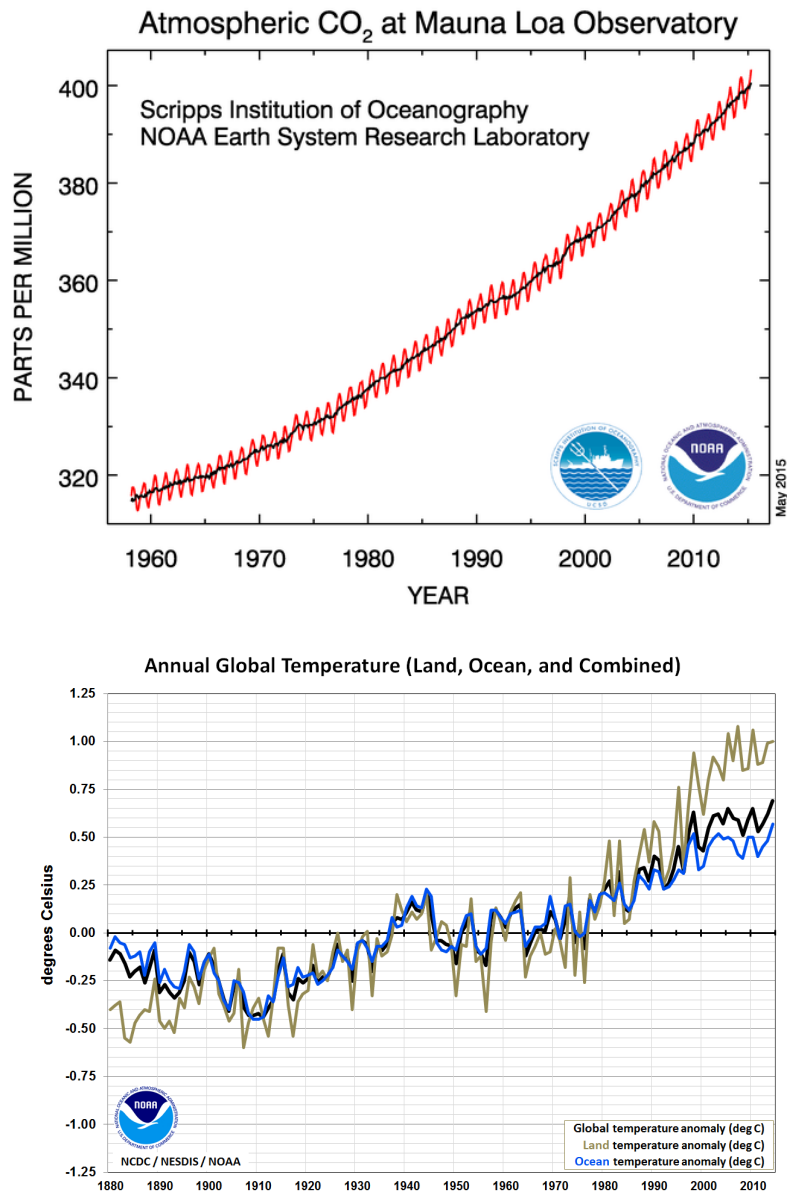


Figure 1.1: Upper panel: CO<sub>2</sub> concentration (ppmv) time series from 1958 to 2015 taken at Mauna Loa, Hawaii.(data website: <http://www.esrl.noaa.gov/gmd/ccgg/trends/>). Lower panel: Temperature time series for land-only (green), ocean-only (blue) and land-and-ocean (black) (data website: <http://www.ncdc.noaa.gov/sotc/summary-info/global/201412>).

**neutral atmosphere** and a conducting atmosphere known as the **ionosphere**. The latter is subdivided in three main layers: i) the D layer from 50 km up to 90-100 km; ii) the E layer, located at 100-150 km and; iii) the F layer, situated at 150-300 km (divided again in F1 and F2 layers).

Another classification of the vertical structure attends to its composition and mixture. In this way the effect of molecular diffusion determines two regions: the **homosphere**, where the mean molecular weight varies little with altitude (from lower altitudes up to 90-100 km) and above, the **heterosphere**, where the mean molecular weight varies with altitude (Brasseur and Solomon, 2005). In the heterosphere, molecular diffusion dominates and the different constituents are layered depending on its molecular weight.

Since temperature is a key parameter to understand the major part of the physical processes in the Earth's atmosphere, the most interesting classification of the vertical structure is based on it (particularly on temperature inversions). Each inversion determines a transition layer between atmospheric regions of a well-defined temperature gradient (Figure 1.2). To better understand this vertical temperature structure, we need to briefly introduce some basic facts of atmospheric dynamics and energy balance.

Approximately 30% of the solar radiation flux is reflected into space, 21% is absorbed by the atmosphere and 49% is absorbed by the Earth's surface (Figure 1.3). The atmosphere is nearly transparent in the visible and hence the visible radiation reach the ground. This incoming energy heats the surface which re-emits it back to the atmosphere as infrared radiation or releases it as latent heat to the lower atmospheric layers. Thus, the lower atmosphere is warmer near the surface and cooler at higher altitudes. Hence there is a negative vertical temperature gradient. Taking into account the hydrostatic equilibrium, there is also a negative vertical pressure gradient. The gradients produce a convective motion with a constant decrease of temperature with altitude of  $\sim 8$  K/km (Houghton, 1986). This region dominated by convective motions is known as the **troposphere** and is where the weather phenomena take place. Because of its nature, the tropospheric extension vary depending on the incoming solar flux. In this way at lower latitudes, the tropospheric convective instability exist up to about 18 km due to the larger solar irradiation. At higher latitudes (polar region), with lower solar irradiance, the upper tropospheric limit extends up to about 8 km. This layer contains around 85% of the total atmospheric mass.

Above the troposphere we find a boundary layer where the first temperature inversion takes place. This layer is called the tropopause and is where the temperature gradient changes its sign from negative to positive. The layer above the tropopause is characterized by a positive temperature gradient due to the absorption of solar UV photons by  $O_3$  in the Hartley ( $\sim 200$ -300 nm) and Huggins ( $\sim 310$ -340 nm) bands. This region is called the **stratosphere** and is where the air layers are quite stable. This fact inhibits the vertical convective motions favoring the horizontal ones. The stratosphere extends from about 10-15 km up to about 50 km. In this layer resides the ozone layer, where the UV radiation, harmful for life, is absorbed.

At 50 km we find another transition layer, the stratopause. At these altitudes the

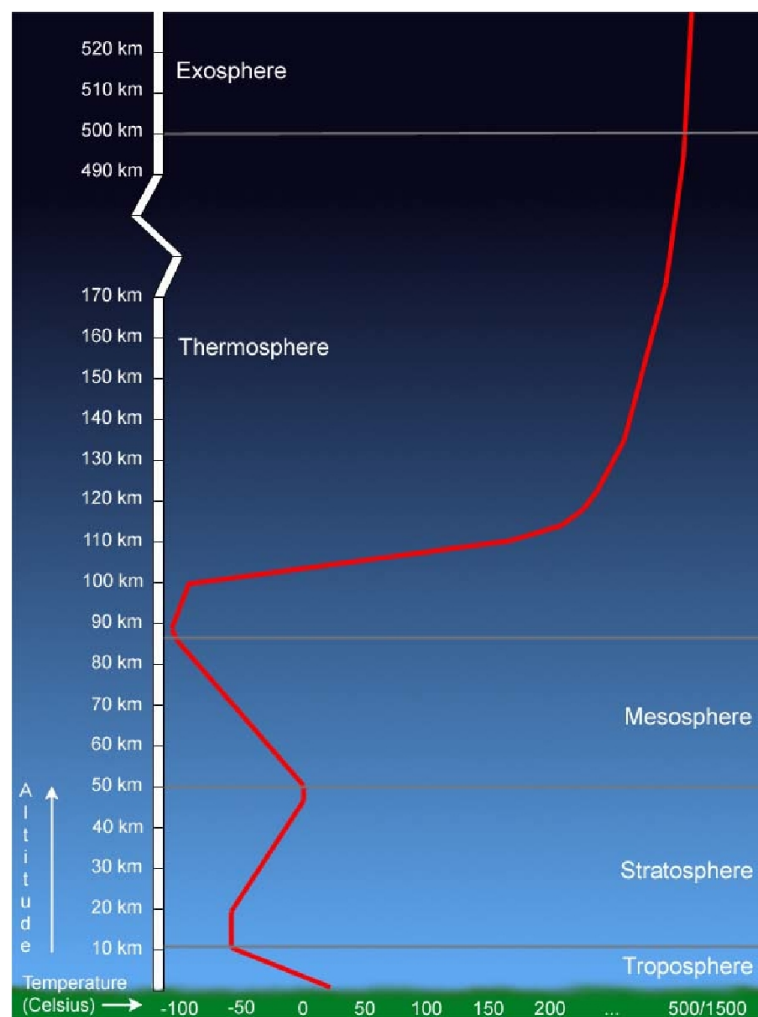


Figure 1.2: Vertical structure of atmosphere based on temperature inversions

temperature gradient become negative again (second inversion point). This occurs because the cooling is greater than the heating. The negative temperature gradient region, known as the **mesosphere**, extends from about 50 km up to about 87 km in the summer pole and up to approximately 100 km in the winter pole. The latter region is called the mesopause, the third inversion point and the coolest region of the atmosphere.

The next positive temperature gradient region is called the **thermosphere** and spans from 80-100 km up to 500-600 km. Here, the absorption of extreme UV solar photons and the interaction with energetic particles cause ionization and photodissociation of O, O<sub>2</sub> and N<sub>2</sub> (these effects are responsible of the temperature increase). During nighttime, the thermospheric temperature is about 400 K (Eddy, 2009). At daytime, the solar heating expands the thermosphere and, depending on the solar activity, the atmospheric temperature can reach values between 700 K to 2000 K (Eddy, 2009). In the region between 200 km to 500-600 km, the air density is so small that there is a balance between the incoming solar radiation and the photons escaping to

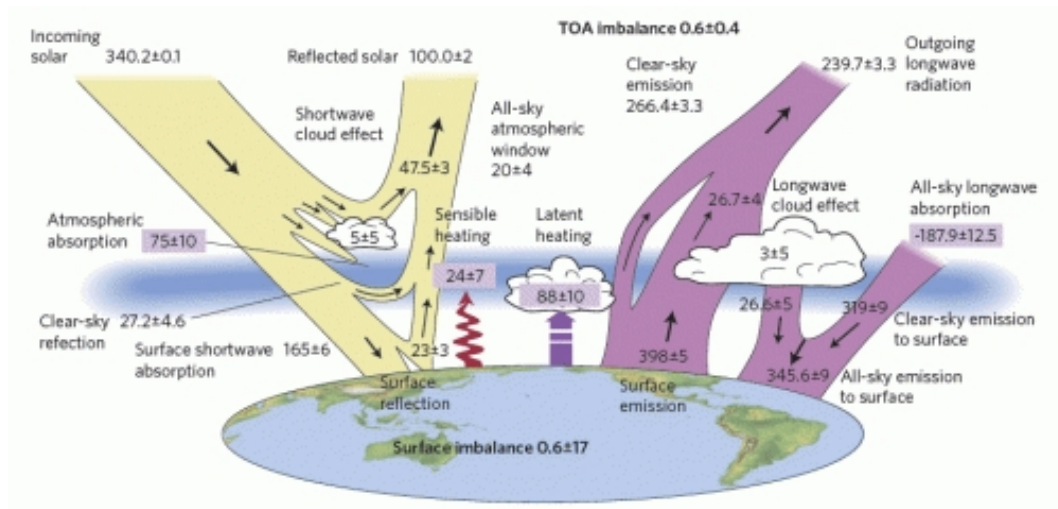


Figure 1.3: The global annual mean energy budget for approximately the 2000-2010 period (Stephens et al., 2012). The fluxes units are  $W \cdot m^{-2}$ . Solar fluxes are in yellow and infrared fluxes in pink.

space. Thus the temperature becomes effectively constant.

The next boundary layer is the thermopause which defines the limit where the solar interaction with the atmosphere ends. Beyond this point, the particles (mostly H and He) move with large mean free paths. This last region is called the **exosphere** and conforms the Earth's last frontier to outer space.

It is also very frequent to find in the atmospheric research literature terms as low, middle and upper atmosphere. Although these terms are not clearly defined, they are often referred to the troposphere (low), to the stratosphere and sometimes to the stratosphere and mesosphere (middle) and to the mesosphere or mesosphere + thermosphere or thermosphere (upper).

### 1.2.3. Composition

The chemical composition of the atmosphere has been varying hand in hand with the evolution of the planet. Different factors, as geology or solar radiation, has been shaping the evolution of the atmosphere until today. Nowadays the two main compounds are molecular nitrogen and oxygen ( $N_2$  and  $O_2$ ) in a ratio of 78% and 21% respectively (Brasseur and Solomon, 2005). The remaining gases like  $CO_2$ ,  $O_3$  or  $CH_4$  are below 1% (Figure 1.4). This composition is modeled mainly by the reaction between its compounds, by interaction with solar radiation (photoionization and photoabsorption) and by atmospheric dynamics.

The main gases ( $N_2$  and  $O_2$ ) have a relatively constant abundance until the photo-dissociation becomes important above approximately 90 km (Brasseur and Solomon, 2005).

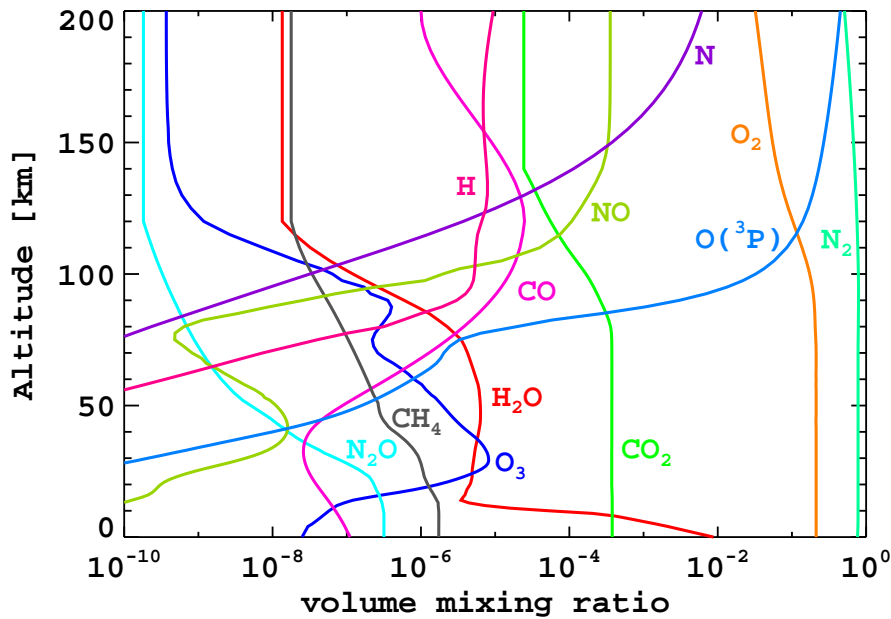


Figure 1.4: Volume mixing ratios of main components of Earth's atmosphere given for usual daytime and mid-latitude conditions from López-Puertas and Taylor (2001).

Water vapour ( $\text{H}_2\text{O}$ ) concentrations are high near Earth's surface because of the proximity of the oceans. At higher altitudes,  $\text{H}_2\text{O}$ , decreases up to the hydropause (Milz et al., 2005). Above, it remains roughly constant up to 70-80 km, where the photodissociation induces another decrease (Brasseur and Solomon, 2005). Water vapour is very important for the study of the radiative balance of the atmosphere because of its strong infrared emissions.

Carbon dioxide ( $\text{CO}_2$ ) has a constant volume mixing ratio up to 70-80 km where it begins to decrease because of molecular diffusion and photodissociation (Garcia et al., 2014). As mentioned before, it is a key gas for understanding the radiative balance and global warming due to its infrared emissions. Its spectroscopic molecular properties are described in detail in the next section.

Other gases like  $\text{CH}_4$  and  $\text{N}_2\text{O}$  are abundant at the surface and their concentrations decrease with altitude due to oxidation and photodissociation. Carbon monoxide ( $\text{CO}$ ) is an important molecule for the tropospheric chemistry. It is produced in the stratosphere and the mesosphere (by the oxidation of methane), and in the lower thermosphere (by  $\text{CO}_2$  photolysis) (Brasseur and Solomon, 2005; Garcia et al., 2014).

Another important source of greenhouse gases are the human activities. As we commented earlier, the industrial development has been increasing their concentrations over the last century.

Although the percentage of atmospheric ozone ( $\text{O}_3$ ) is less than 1%, it plays an important role in the energy budget, the chemistry and composition of the atmosphere, particularly in the stratosphere and upper mesosphere (Brasseur and Solomon, 2005). The absorption of ultraviolet solar radiation by  $\text{O}_3$  in the stratosphere acts as shield

for life on the surface and produces the high temperatures of the stratosphere. Ozone also produces an important cooling that affects critically to the thermal structure and hence to the radiative balance. The ozone abundance below 30 km is variable due to atmospheric dynamics. In this region it is produced by photodissociation of  $O_2$  and recombination with atomic oxygen (Chapman, 1930). The  $O_3$  density maximum is located at approximately 25 km. At higher altitudes it decreases due to photodissociation. At 80 km,  $O_3$  increases again because of the presence of atomic oxygen.

$NO$  and  $NO_2$  (known as  $NO_x$ ) are very important constituents, contributing to ozone destruction due to their catalytic cycle (Brasseur and Solomon, 2005). Nitric oxide ( $NO$ ) plays also an important role in the thermospheric cooling, particularly during auroral events (Kockarts, 1980). In addition,  $NO$  is an important source of ionization in the ionosphere, particularly in the D and E regions (Barth et al., 2009).

#### 1.2.4. Energy Balance

The Earth's energy balance consists in the difference of the energy fluxes between the incoming solar radiation and the outgoing (mainly terrestrial) radiation. The atmosphere, the clouds or the surface reflects, absorbs or re-emits the energy incoming from the Sun or the Earth's atmosphere itself (see Fig. 1.3).

The incoming solar radiation (Figure 1.5a) has an approximate spectral shape of a black body at  $\sim 6000$  K. Its major spectral contribution extends from 200-250 nm to 1300-1700 nm and peaks at  $\sim 500$  nm. As mentioned earlier, the major part of the incoming radiation reaching the surface is within the visible part of the spectrum. On a global average, 30% of the incoming energy is reflected back to space (albedo). Another 21% is absorbed by the atmosphere and the Earth's surface absorbs the remaining 49% of the total solar radiation. The surface re-emits the absorbed solar radiation as infrared radiation and also by transferring latent heat to the atmosphere. A fraction of the infrared emission is radiated to outer space but the major part is absorbed in the atmosphere by molecules with strong vibration-rotational bands, the greenhouse gases (water vapour,  $CO_2$ ,  $O_3$ ,  $CH_4$  and  $N_2O$ ). The total outgoing infrared radiation (Fig. 1.5a) can be described as a black body at an approximate temperature of 250 K.

In the thermosphere,  $O$ ,  $N_2$  and  $O_2$  absorb the photons with wavelengths shorter than 102.5 nm producing photodissociation and ionization. At larger wavelengths (UV),  $O_2$  absorbs in the Schumann-Runge continuum (100-175 nm), in the Schumann-Runge bands (175-205 nm) and more weakly in the Herzberg continuum (Figs. 1.5b, and 1.5c) (Mlynczak and Marshall, 1996; López-Puertas and Taylor, 2001; Brasseur and Solomon, 2005).

The thermosphere can be also heated by quenching of  $O(^1D)$  (through  $N_2$ ) and  $O_2$  and by collisions between ambient electrons and ions and neutrals. Regarding the mesospheric radiative heating, it is produced by the absorption in the  $O_3$  Hartley bands (24.2-31.0 nm) and  $O(^1D)$  quenching following the  $O_3$  and  $O_2$  photolysis.

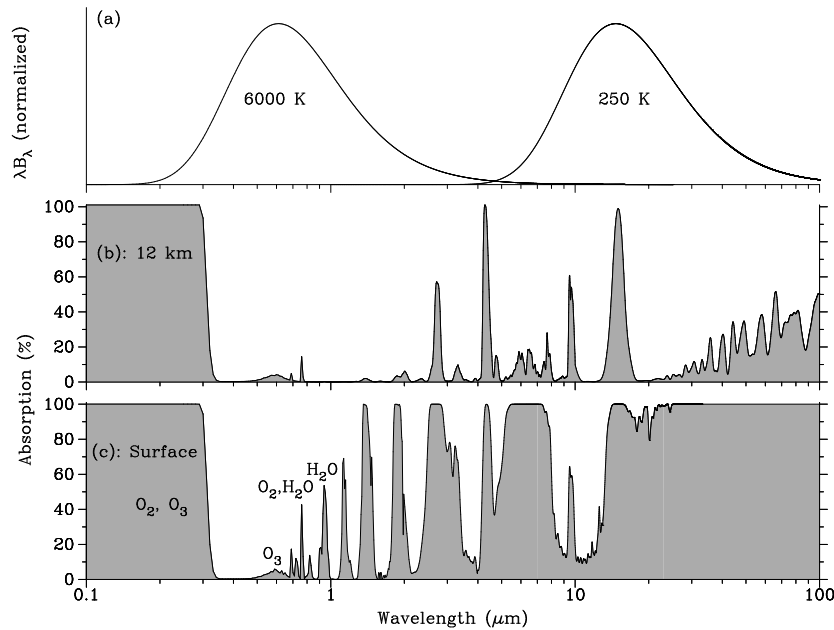


Figure 1.5: Atmospheric absorption: (a) The blackbody emission curves for 6000 K (symbolizing the Sun emission) and 250 K (symbolizing the terrestrial emission) normalized to the energy emitted. (b) Absorption spectra of the atmosphere for 12 km to its upper part. (c) Atmospheric absorption spectra at the surface. (López-Puertas and Taylor, 2001)

With respect to cooling mechanisms, emissions of NO at 5.3  $\mu\text{m}$  (most important around 120–200 km), of  $\text{CO}_2$  at 15  $\mu\text{m}$  (further explained below), and of O at 6.3  $\mu\text{m}$  are the most important in the thermosphere (López-Puertas and Taylor, 2001; Mlynczak et al., 2010, 2014). In the mesosphere, the 15  $\mu\text{m}$   $\text{CO}_2$  emission is the most important and, to a lesser extent, 9.6  $\mu\text{m}$  emissions from  $\text{O}_3$  (López-Puertas and Taylor, 2001; Brasseur and Solomon, 2005). Above 140 km, it is important to take into account the cooling by downward molecular heat conduction.

There are other important heating mechanisms like that produced by the exothermic chemical reactions (chemical heating) (Mlynczak and Solomon, 1993; Smith et al., 2015) (see, also tables of neutral and ion-chemistry involving nitrogen and oxygen in Roble (1995)), and Joule dissipation<sup>3</sup> of ionospheric currents (upper atmosphere). Dynamic effects contribute also to the heating of the mesosphere and lower thermosphere by dissipation of tides, planetary and gravity waves originated in the lower atmosphere or by adiabatic compressions due to vertical motions. For example, the tides propagating from below generate pressure gradients that force the gas of the thermosphere into motion following negative temperature gradients (Fuller-Rowell, 1995). A very good overview of the energetics of the middle and upper atmosphere can be found in the book edited by Siskind et al. (2000).

<sup>3</sup>Joule heating is caused by frictions associated to collisions between neutral and ions due to the presence of electric fields (see Rees, 1989).



### 1.3. Carbon Dioxide

Historically, carbon dioxide was identified in 1757 by the Scottish physician and chemist Joseph Black (he called it *fixed air*). The molecule is formed by two carbon atoms and one oxygen atom linked by 116.3 pm symmetric covalent bonds (Figure 1.6). CO<sub>2</sub> is a colorless and odorless gas with a molar mass of 44.01 g mol<sup>-1</sup>, a density of 1.977 kg m<sup>-3</sup> (at 1 atm and 0°C), a melting point of 216.6 K, a sublimation point at 194.7K (at 1 atm) and with no permanent dipolar moment. At present, it forms the 0.0596%<sup>4</sup> of the total mass of atmospheric air.



Figure 1.6: CO<sub>2</sub> structural formula showing the covalent bonds length.

The abundance of *natural* CO<sub>2</sub> is controlled by the carbon cycle: A biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the Earth. The *anthropogenic* CO<sub>2</sub> comes mainly from the use of fossil fuels in transportations and from the activity of different industries like iron and steel production or cement manufacturing.

#### 1.3.1. Spectroscopy and energy levels

There are three kinds of internal energy transitions: rotational, vibrational and electronic transitions. The ro-vibrational and pure rotational transitions establish the near and middle infrared spectrum. The electronic ones, with highest energy values, are located in the visible and in the ultraviolet. We consider here only the infrared emissions. The CO<sub>2</sub> does not have a pure rotational spectrum because it does not have a permanent dipolar moment.

Let us briefly summarize the theory of the rotational energy spectra. Since CO<sub>2</sub> is a linear molecule, it can be modeled using the *rigid rotator* model. This model assumes that the molecule is composed of two different masses linked by a rigid bond of distance  $r^5$ . The moment of inertia is  $I = mr^2$ , where  $m = m_1m_2/(m_1+m_2)$  is the *reduced mass*. Taking into account the solution for the time-independent Schrödinger equation for this system:

$$\Psi_{J,M} = \sqrt{\frac{(2J+1)(J-|M|)!}{4\pi(J+|M|)!}} e^{im\phi} P_J^{|M|}(\cos\theta) \quad (1.1)$$

where  $\theta$  and  $\phi$  are the polar and azimuthal angles of the spherical coordinates,

<sup>4</sup>Source: NOAA Earth System Research Laboratory

<sup>5</sup>Since the coordinate  $r$ , is taken to be constant ( $r_0$ ), the partial derivatives with respect to  $r$  are zero. Thus,  $r$  does not appear as a variable in the wave functions.



$P_J^{|M|}(\cos\theta)$  are the associated Legendre polynomials, and  $J$  and  $M$  are quantum numbers representing the total angular momentum and its component along the polar axis, respectively. Thus, the energies of the different rotational transitions are:

$$E_J = BJ(J+1) \quad J = 0, 1, 2, \dots \quad (1.2)$$

where  $B = \hbar/(2I)$  is the rotational constant ( $\hbar$  is the reduced Planck constant). The symmetry of the wave functions  $\Psi_{J,M}$  characterize the selection rule for transitions  $J' - J''$  between two levels. Given the selection rule  $\Delta J = J' - J'' = \pm 1$ , the energy involved in a transition is:

$$E_{J+1} - E_J = 2B(J+1). \quad (1.3)$$

In the *non-rigid rotator* model the bond forces are assumed to depend linearly on the distance. The energy of the system is:

$$E_J = BJ(J+1) - DJ^2(J+1)^2, \quad (1.4)$$

where  $D$  is the *centrifugal distortion constant* ( $\hbar^2/\sqrt{2kmr_0^3}$  with  $k$  as the force constant).

For the vibrational levels, to describe the lower excitation transitions, we can use the *Born-Oppenheimer approximation*<sup>6</sup>. The interaction energy,  $V(r)$ , can be expressed in the form of a MacLauren series taking the zero of potential energy at  $r = r_0$  (where  $dV/dr = 0$  and  $V(0)=0$ ), thus:

$$V(r - r_0) = \frac{1}{2} \left[ \frac{d^2V}{dr^2} \right]_{r=r_0} (r - r_0)^2 + \text{higher order terms}. \quad (1.5)$$

For the transitions between lower energy states, higher order terms of the equation can be truncated. In this case, taking the first term of the equation, we are approximating the potential energy curve by a parabolic function. This is known as the *harmonic oscillator approximation*. With the Schrödinger equation we obtain the quantized energy expression by:

$$E = \left( v + \frac{1}{2} \right) \nu_v \quad (1.6)$$

where  $v$  is the quantum number associated with a given vibrational level and  $\nu_v = \hbar\sqrt{\frac{k}{m}}$  is called the *fundamental frequency*. Since the selection rule is  $\Delta v = \pm 1$ , the energy involved in a transition is:

$$E' - E'' = \left[ \left( v' + \frac{1}{2} \right) - \left( v'' + \frac{1}{2} \right) \right] \nu_v = \Delta v \nu_v = \nu_v \quad (1.7)$$

<sup>6</sup>The *Born-Oppenheimer approximation* allows the use of wave function of the molecule as two wave functions (electronic and molecular),  $\Psi_{total} = \Psi_{electr} \times \Psi_{molec}$ .

For higher excitation transitions, we cannot use neither the *harmonic oscillator* nor the *Born-Oppenheimer* approximations. Thus we will use the *anharmonic oscillator* model. The energy can be calculated with the (Equation 1.5), just taking the two first terms

$$E = \left(v + \frac{1}{2}\right) \nu_v - \left(v + \frac{1}{2}\right)^2 \chi \nu_v \quad (1.8)$$

where  $\chi$  is the *anharmonicity constant*. The selection rule is  $\Delta v = \pm 1, \pm 2$ .

In the case of polyatomic molecules, the vibration modes can be treated as the sum of normal vibrations. For  $\text{CO}_2$  there are three fundamental vibrational modes:  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  (Figure 1.7). The first is the symmetric stretch ( $\nu_1$ ) and neither has absorption nor emission in infrared because there is no dipolar momentum variation associated with its motion. The other two are:

- *Bending stretch mode*  $\nu_2$ : Selection rule  $\Delta J = 0, \pm 1$ . It is degenerated twice because the movement can happen in the two perpendicular directions.
- *Asymmetric stretch mode*  $\nu_3$ : Selection rule  $\Delta J = \pm 1$ . Known as the parallel mode, its dipolar moment does vary along the internuclear axis.

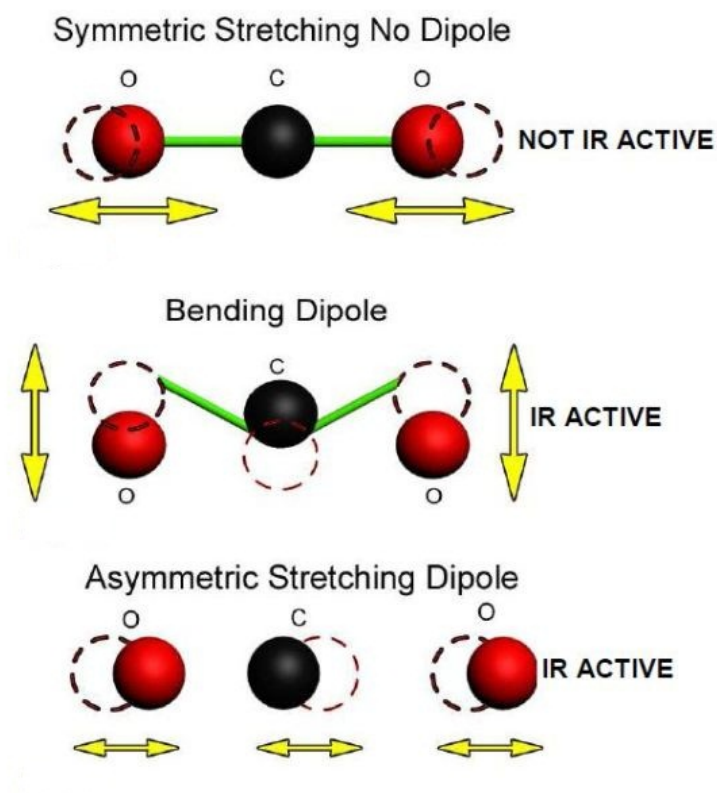


Figure 1.7:  $\text{CO}_2$  fundamental vibrational levels.

The vibration-rotation transitions of these modes are the most important ones for the description of the CO<sub>2</sub> spectrum in the IR and NIR. For the asymmetric stretch mode ( $v_3$ ), if  $v_2=0$ , due to the selection rule  $\Delta J = \pm 1$ , the  $v_3$  spectra will show two branches with the following line center frequencies:

$$\text{R branch: } \nu(J) = \nu_0 + 2B(J+1) \quad \text{for } \Delta J = +1 \quad (1.9)$$

$$\text{P branch: } \nu(J) = \nu_0 - 2BJ \quad \text{for } \Delta J = -1. \quad (1.10)$$

On the other hand, the bands of the  $v_2$  bending mode (selection rule  $\Delta J = -1, 0, 1$ ) have P, Q, and R branches.

The transitions between the ground vibrational state and the first vibrationally excited modes ( $v_i = 1$ ) are called *fundamental* transitions or bands and are, by far, the strongest. The bands with lower vibrational state different from the ground state are often known as *hot* bands. The reason is because they occur more profusely in hot gases. For CO<sub>2</sub>, hot bands are of special significance in atmospheric regions where non-LTE processes populate the higher vibrational levels (see Fig.1.8). The transitions occurring between the excited vibrationally states with quantum number larger than one and the ground state are usually called *overtones*. Furthermore, the bands that take place between vibrational levels that differ in more than one vibrational quanta are called *combinational* bands.

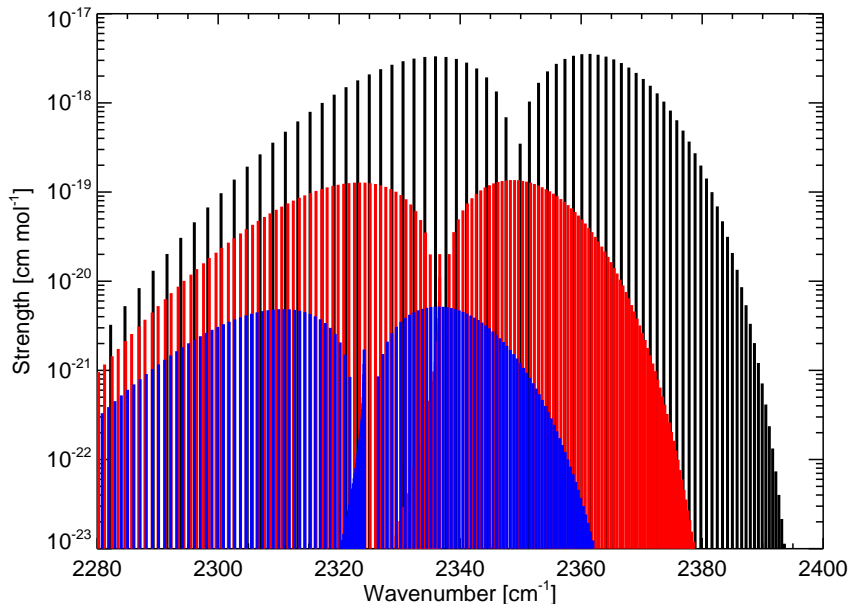


Figure 1.8: CO<sub>2</sub> transition lines from the fundamental  $00^0 1 \rightarrow 00^0 0$  (black), first hot  $01^1 1 \rightarrow 01^1 0$  (red) and second hot  $02^2 1 \rightarrow 02^2 0$  (blue) bands in the 4.3  $\mu\text{m}$  region. Data from HITRAN 2004 database (Rothman et al., 2005).

### 1.3.2. CO<sub>2</sub> Cooling and Heating

The most important cooling mechanism of the stratosphere, mesosphere and lower thermosphere is the CO<sub>2</sub> 15 μm emission (López-Puertas and Taylor, 2001; López-Puertas and Funke, 2015). The respective cooling rate depends on two very variable parameters: the kinetic temperature and the CO<sub>2</sub> abundance. Hence, we must consider a range of global and seasonal conditions. In addition, it depends also on the rate coefficient for the collisional deactivation of CO<sub>2</sub>(0,1<sup>1</sup>,0) by atomic oxygen ( $k_{CO_2-O}$ ) and on the O(<sup>3</sup>P) number density.

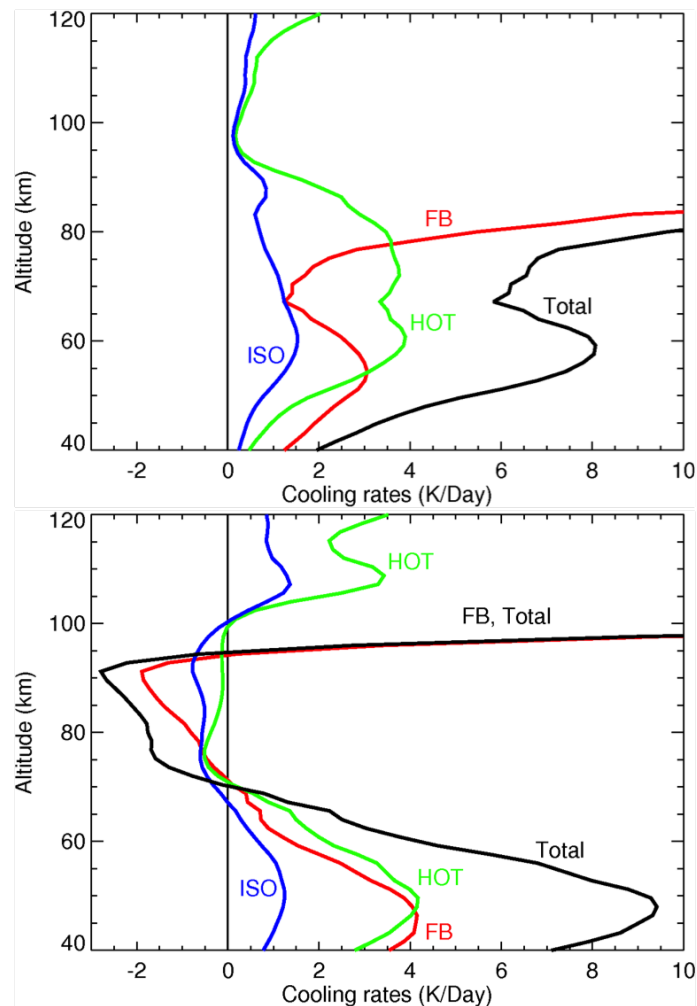


Figure 1.9: Upper panel: 15 μm bands cooling rate in polar winter. Lower panel: 15 μm bands cooling rate in polar summer. The profiles represent calculated cooling for the fundamental (red line), the 3 first hot bands and the 7 second hot bands for the 626 isotope (green line), and the fundamental bands of the minor isotopes 636, 628 and 627 (blue line) (López-Puertas and Taylor, 2001).

Analyzing the contributions of the CO<sub>2</sub> bands to the cooling in the stratosphere and the mesosphere, we find that it is driven by the optically thin isotopic and hot

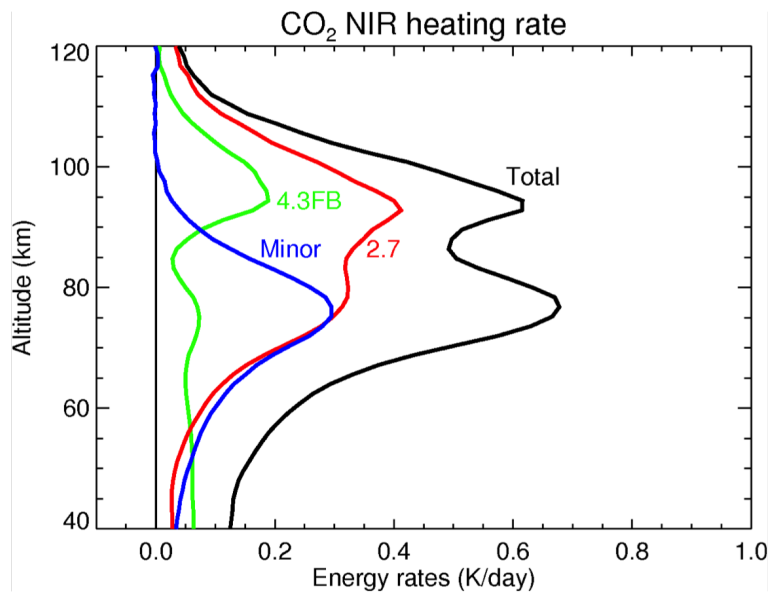


Figure 1.10: Heating rates profiles integrated over one day in winter conditions (30°N) for the energy initially absorbed in the CO<sub>2</sub> 2.7 μm band (red line), 4.3 μm fundamental band of the 626 isotope (green line) and the 2.0 and 4.3 μm isotopic and hot bands (blue line) (López-Puertas and Taylor, 2001).

bands (principally the first hot) rather than the strong fundamental band. In these regions the maximum cooling ranges from  $-2$  to  $10$  K/day and depends on temperature (López-Puertas and Taylor, 2001). In the lower thermosphere the cooling is driven by the fundamental band with a significant contribution from the first hot band. One of the most interesting feature is the large increase of the cooling rate in summer conditions compared to winter (Figure 1.9).

The near-infrared CO<sub>2</sub> bands contribute significantly to the atmospheric heating of the mesosphere. This heating is mainly induced by solar absorption in the bands around 2.7 and 4.3 μm during daytime (López-Puertas and Taylor, 2001; Fomichev et al., 2004). Most of the energy absorbed by the atmospheric CO<sub>2</sub> in these bands is re-emitted back to space and only a little fraction causes a net heating<sup>7</sup>. Even though it is still significant. The overall CO<sub>2</sub> heating averaged over a full day, adding the 2.0, 2.7 and 4.3 μm contributions, shows a double-peak structure with values close to 0.5 K/day (Figure 1.10). The upper one, around 90 km, is due to the 4.3 μm fundamental band and 2.7 μm bands and the lower one, around 80 km, is due to the 2.7 μm bands, the weaker 2.0 μm bands and the hot and isotopic 4.3 μm bands.

<sup>7</sup>Net heating: The difference between the amount of incoming solar radiation and the amount heat radiated by the Earth back to space.

### 1.3.3. Measurements of CO<sub>2</sub> Abundances in the Middle and Upper Atmosphere

CO<sub>2</sub> is well mixed in the atmosphere with an almost constant mixing ratio up to the upper mesosphere. As we mentioned before, this "constant" mixing ratio with altitude is being increased by anthropogenic emissions (Figure 1.1a). Above this region, i.e. above 80 km, it begins to decrease because of diffusive separation, UV photodissociation and by chemical reaction with O<sup>+</sup>. In the following we review the CO<sub>2</sub> measurements in the middle and upper atmosphere.

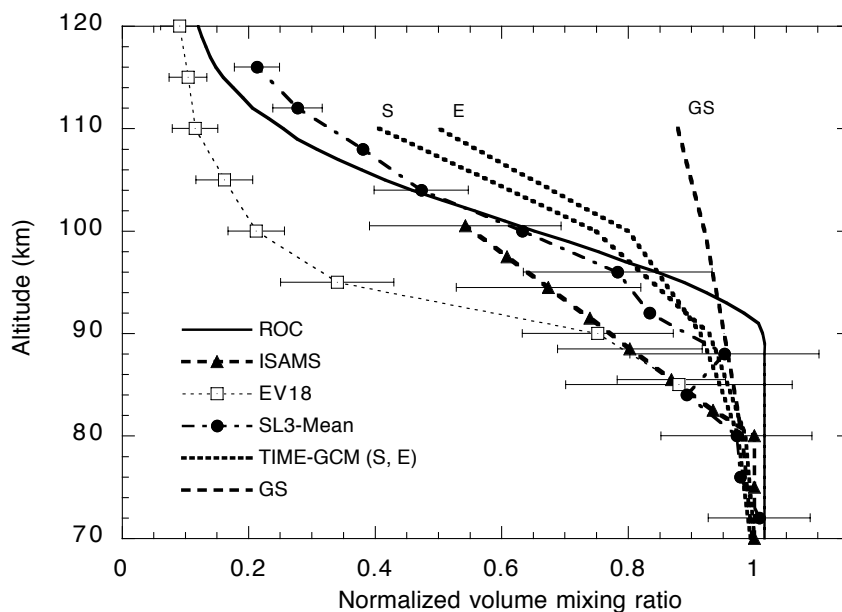


Figure 1.11: CO<sub>2</sub> vertical profiles comparison from different observations by rocket-borne mass spectrometers (ROC), ISAMS, Grille (EV-18) and ATMOS (SL3-Mean). Vertical profiles from two models are shown: NCAR TIME-GCM (E for equinox and S for solstice conditions) and the Garcia-Solomon two-dimensional model (López-Puertas et al., 2000). The profiles are normalized to their respective values in the lower region.

Despite its importance in the middle atmospheric infrared energy balance, CO<sub>2</sub> has been scarcely measured, there. CO<sub>2</sub> was first measured in the upper atmosphere by *in situ* measurements carried out by rocket-borne mass spectrometers (Figure 1.11). The first time it was measured was at nighttime from 120 to 140 km (Offermann and Grossmann, 1973). Different *in situ* measurements were performed during the seventies and in the early eighties by Trinks and Fricke (1978) and Trinks et al. (1978) during the Aladdin 74 campaign and by Offermann et al. (1981). The CO<sub>2</sub> vmr profiles obtained at that time were approximately constant ( $335 \pm 50$  ppmv) up to about 90 km where it starts dropping rapidly with altitude. The errors of these measurements were of the order of 20-30% (López-Puertas et al., 2000). Beyond this epoch two different methods (techniques) were used to measure CO<sub>2</sub>: solar occultation and infrared emission.

The Grille spectrometer aboard Spacelab 1 used solar occultation taking infrared limb spectra at sunrise and sunset in 1983. CO<sub>2</sub> abundances were measured in the mesosphere and lower thermosphere in four occultations. The results showed a lower CO<sub>2</sub> in the 90-110 km region (Figure 1.11) (Vercheval et al., 1994; Girard et al., 1988). The Atmospheric Trace Molecule Spectroscopy (ATMOS) on Spacelab 3 obtained IR occultation spectra in the troposphere-lower thermosphere region in 1985. In addition the kinetic temperature and pressure profiles were obtained. CO<sub>2</sub> mixing ratios were retrieved by Rinsland et al. (1992) from 70 km up to 116 km, with an average 320 ppmv in 70-90 km, and a decrease around 90 km in the southern hemisphere and around 100 km in the northern hemisphere (Figure 1.11) (López-Puertas et al., 2000).

Regarding CO<sub>2</sub> 4.3 μm emissions it is worth mentioning some constrains affecting its measurements. There are uncertainties in the modelling of the non-LTE populations of the emitting levels. As explained in Chapter 5, for 4.3 μm it is important to take into account collisional processes like the CO<sub>2</sub>(ν<sub>3</sub>) with N<sub>2</sub>(1) or the excitation of N<sub>2</sub> through O(<sup>1</sup>D). The 15 μm emission is strongly affected by kinetic temperature, pressure, atomic oxygen and collisions of CO<sub>2</sub>(010) with O(<sup>3</sup>P) above 100 km. The Spectral Infrared Rocket Experiment (SPIRE) measured limb radiance from 15 and 4.3 μm bands at tangent heights from 50 up to 150 km. SPIRE had a radiometric calibration error of ± 25% (Stair et al., 1985). The CO<sub>2</sub> from SPIRE 15 μm measurements are consistent with other rocket experiments and with the lower CO<sub>2</sub> values encountered at 80-110 km. For example, Wintersteiner et al. (1992) analysed the 15 μm measurements using pressure, kinetic temperature and atomic oxygen from MSIS-86 and adjusting the collisional parameter  $k_{CO_2-O}$ . They find the best overall fit using a value for this rate of  $5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K and the CO<sub>2</sub> rocket measurements. The depletion of CO<sub>2</sub> vmr in the 80-110 km region fits the SPIRE observations for a  $k_{CO_2-O}$  value of  $6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K (20% higher).

Nebel et al. (1994) studied the SPIRE 4.3 μm daytime measurements that found that they are consistent with the CO<sub>2</sub> rocket measurements up to 110 km. Above this altitude up to 130 km, the measurements are clearly underestimated by a factor of 2. As we mentioned before, measurements are constrained by uncertainties in the non-LTE excitation processes.

The Spectroscopic Infrared Structure Signatures Investigation (SISSI), measured 15 and 4.3 μm zenith radiances in four rocket experiments (between 1990 and 1991) during twilight. This instrument measured simultaneously kinetic temperature, pressure and O(<sup>3</sup>P) number density although with considerable errors (± 10% for kinetic temperature and ± 30% for atomic oxygen). The radiance measurements themselves presented errors of ± 30% (Vollmann and Grossmann, 1997). They fit the 4.3 μm radiance below 100 km according to previous rocket measurements by multiplying it by 2.5 and by 4 above 105 km. Regarding 15 μm, the radiance was also explained but have to decrease the  $k_{CO_2-O}$  rate to  $\sim 1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K (notably lower than that required in SPIRE). The increase in the 4.3 μm radiances above 105 km<sup>8</sup> may be caused by an unidentified non-LTE source (e.g., NO<sup>+</sup>(ν<sub>3</sub>)). The 15 μm band

<sup>8</sup>Nebel et al. (1994) and López-Puertas et al. (1998b) found similar increases in SPIRE and ISAMS measurements, respectively.

emission would also be consistent with rocket measurements if  $k_{CO_2-O}$  values are between  $3 - 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K (more consistent also with SPIRE results).

The first global measurements of  $CO_2$   $4.3 \mu\text{m}$  were performed by the Stratospheric and Mesospheric Sounder (SAMS) on Nimbus 7 between 1978 and 1981 by using the pressure modulation technique. López-Puertas and Taylor (1989) and López-Puertas et al. (1998b) analysed daytime data using simultaneous measurements of kinetic temperature and pressure up to 60 km and using the CIRA 72 climatology above that altitude. The best radiance agreement gave a  $CO_2$  vmr profile notably lower than rocket measurements in the 80-95 km region (López-Puertas et al., 2000).

The Improved Stratospheric and Mesospheric Sounder (ISAMS) aboard Upper Atmosphere Research Satellite (UARS) carried out  $4.6 \mu\text{m}$  global measurements from around 10 km up to 105 km during six months. The main ISAMS improvements with respect to SAMS are: i) more sensitivity to the second  $CO_2$  isotope (636) emissions; ii) better signal to noise ratio ( $\sim 1$  up to 120 km) and; iii) simultaneous measurements of temperature and pressure up to 80 km. López-Puertas et al. (1998b) and Zaragoza et al. (2000) performed a detailed analysis of the  $4.3 \mu\text{m}$  daytime emission. These studies showed that the  $CO_2$  vmr profile does not change (within ISAMS uncertainties) with latitude or season up to 100 km during daytime (Figure 1.11).

The Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA), a limb scanning instrument on board two space shuttle missions, measured the  $4.3 \mu\text{m}$  emissions with global distribution in 1994 and 1997. Kaufmann et al. (2002) retrieved  $CO_2$  number densities by analyzing daytime radiance from 60 km up to 130 km. Considering the optical thickness of  $4.3 \mu\text{m}$  radiances between 75 km and 110 km and the excitation of  $N_2$  through  $O(^1D)$  uncertainties, the systematic error of the retrieved  $CO_2$  was within the range of 10-20%. The  $CO_2$  falloff of CRISTA, where diffusive separation starts, is situated at 70-80 km, lower than from rocket measurements, ATMOS and ISAMS measurements (Figure 1.12). Above this altitude, the mean CRISTA  $CO_2$  vmr results are lower than SAMS and ISAMS in the 80-100 km region and than ATMOS  $CO_2$  between 80 km and 120 km.

The Fourier Transform Spectrometer on the Canadian Atmospheric Chemistry Experiment (ACE-FTS) aboard SCISAT-1 satellite measured by solar occultation the  $CO_2$  in mesosphere and lower thermosphere. ACE  $CO_2$  vmr shows the falloff at 70-80 km with higher values than CRISTA above 70 km, slightly higher values than those of ISAMS in 80-100 km and lower than rocket measurements (Beagley et al., 2010).

More recently, the Sounding of the Atmosphere using Broadband Emission Radiometry (SABER) on board the NASA Thermosphere Ionosphere Energetics and Dynamics (TIMED) satellite has been measuring  $CO_2$   $4.3$  and  $15 \mu\text{m}$  limb emission radiances in the mesosphere and lower mesosphere. Rezac et al. (2015) presented a simultaneous  $T_k/CO_2$  non-LTE retrieval and its application to the whole "13-plus" years of SABER daytime measurements. The total uncertainty in the unconstrained  $CO_2$  vmr retrieval takes the following values: 35% at 70 km, 12% at 90 km, 32% at 110 km (where the  $O(^1D)$  sensitivity maximum is) and 22% at 130 km. The global mean of the  $CO_2$  vmr profiles seems to be well mixed up to 80-85 km. Considering equinox conditions, the  $CO_2$  vmr depart from a well mixed value from 65 to 70 km at high and mid-latitudes.



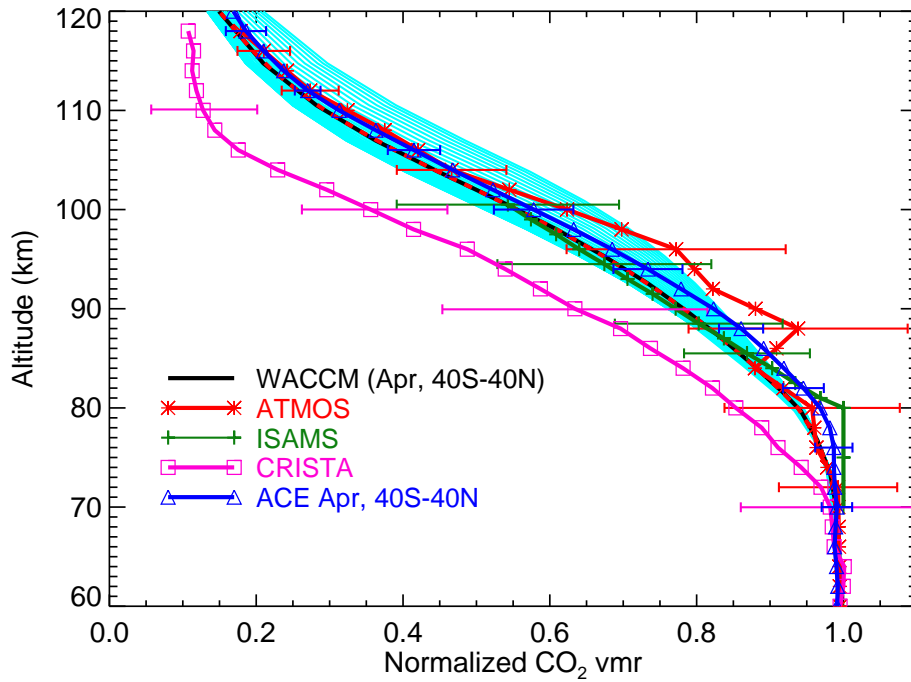


Figure 1.12: Comparison of observational vertical profiles from ATMOS, ISAMS, CRISTA and ACE and modeled vertical profiles from SD-WACCM (setting the Prandtl number in 4). SD-WACCM data is shown as a black line (mean of all models profiles) and as a blue shaded area (profiles in the latitude range of 40°S-40°N). The data have been normalized to the mixing ratio at 60 km (Garcia et al., 2014).

Regarding summer hemisphere solstice, the CO<sub>2</sub> vmr is well mixed up to 87-90 km. A detailed comparison of the ACE and SABER CO<sub>2</sub> measurements with those retrieved in this work are presented in Chapter 6.

Although not studied in this work, we give, for completeness, a brief summary of the most recent measurements of CO<sub>2</sub> vmr in the lower atmosphere. Foucher et al. (2011) presented 5 years (2004-2008) of monthly mean CO<sub>2</sub> vertical profiles from ACE-FTS measurements in the 5-25 km altitude range. These vertical profiles are averaged over 10° latitude bands for Northern mid-latitudes. These measurements show a 'significant' variation with altitude ( $\sim 0.1$  ppmv/km) and a notable seasonal variability of 5 ppmv (1.2%)<sup>9</sup>. Comparisons with in-situ aircraft measurements from the CONTRAIL (Sawa et al., 2008), CARIBIC (Schuck et al., 2009) and SPURT (Gurk et al., 2008) campaigns show that ACE-FTS concentrations are consistent with them in the Northern Hemisphere mid-latitudes. However the stratospheric seasonal cycle amplitude seems to be slightly overestimated.

<sup>9</sup>Note these changes are much smaller than the variations at higher altitudes described above.

## 1.4. Motivation and Objectives

Let us begin describing the state of the art on our current understanding of the role of CO<sub>2</sub> in the middle atmosphere. As mentioned before, CO<sub>2</sub> is a key element for understanding the Earth's energy balance, playing an essential role in the cooling and heating of all atmospheric regions and therefore on its temperature structure. Another important fact is the anthropogenic increase of CO<sub>2</sub>, registered by the Keeling curve, which has a major impact on the atmosphere, including the upper atmosphere. Thus, the CO<sub>2</sub> cooling fingerprint has been observed as a negative trend of mesospheric temperature affecting its thermal structure (Beig et al., 2003) and the drop of the ionospheric F2-layer (Rishbeth, 1990).

Along that line, Emmert et al. (2010) suggested that during the 2008 solar minimum, the increase of CO<sub>2</sub> may have partially produced a low thermospheric density peak, induced by a faster CO<sub>2</sub> cooling of the mesosphere and lower thermosphere (see Fig. 1.13).

Beagley et al. (2010) proposed a new CO<sub>2</sub> loss process (sequestration in dust) around the mesopause as a possible explanation for the overestimation of the CMAM 3D simulations of the ACE CO<sub>2</sub> measurements. However, Garcia et al. (2014) have shown more recently that the ACE CO<sub>2</sub> distributions can be explained by the WACCM model without the need of invoking a new CO<sub>2</sub> loss mechanism.

Emmert et al. (2012) have studied the trends of CO<sub>x</sub> (CO<sub>x</sub> = CO + CO<sub>2</sub>) in the mesosphere and lower thermosphere in the ACE CO and CO<sub>2</sub> observations. They have found a notably large growth rate of CO<sub>2</sub> in this region, larger than expected from the CO<sub>2</sub> increase by human activities in the troposphere (Figure 1.14). In the altitude range of 90-105 km, the ACE-FTS trends are 5-10 ppm per decade larger than predicted by the NCAR global mean model (Figure 1.15).

Yue et al. (2015) have very recently analyzed the trends of CO<sub>2</sub> in the mesosphere and lower mesosphere using SABER measurements from 2002 to 2014. They have found a trend of ~5% per decade at ~80 km and below. Above 80 km the trend, larger in the northern hemisphere mesopause, can be as large as ~12% per decade at 110 km, thus confirming the previous finding of Emmert et al. (2012).

These studies suggest that a more precise knowledge of the spatial-temporal distribution of CO<sub>2</sub> in the mesosphere and thermosphere is needed in order to understand better the energy balance of this region, its dynamical coupling to the regions below, and its response to anthropogenic changes.

Historically, global CO<sub>2</sub> measurements in the mesosphere and lower thermosphere have been limited. In the last few years, instruments like ACE (Beagley et al., 2010), SABER (Brown et al., 2006) and MIPAS (Fischer et al., 2008) have contributed to provide a global view of these regions. Compared to ACE, an occultation instrument, MIPAS has the advantage of providing global latitudinal (pole-to-pole) and seasonal measurements. Compared to SABER, a wide band limb emission radiometer, MIPAS measured high resolution limb emission spectra and in a wide spectral coverage. Thus, MIPAS is able to discriminate the contributions of the many CO<sub>2</sub> bands that

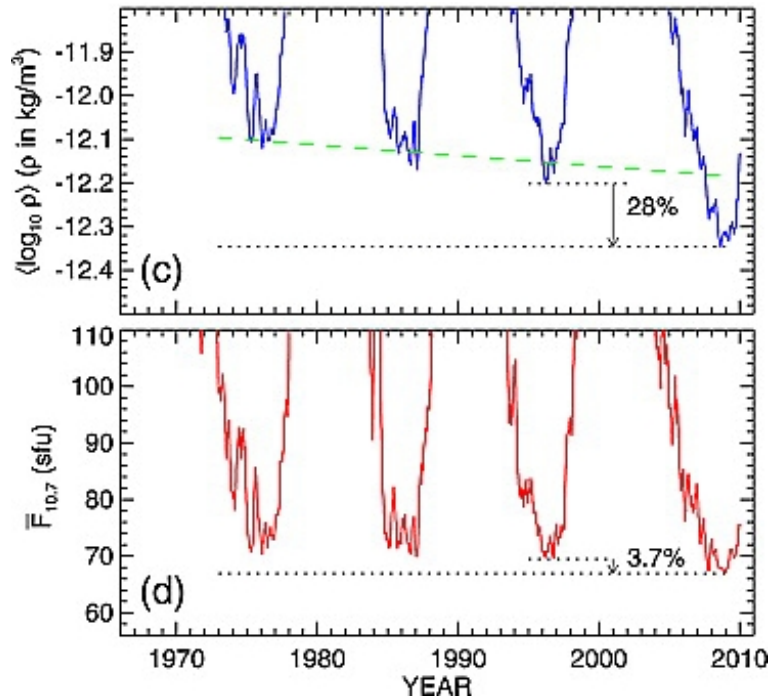


Figure 1.13: Upper panel: 81-day global average logarithmic densities at a fiducial altitude of 400 km. Green dashed line indicates the solar minimum. Black dotted represents the overall density minimum. Lower panel: 81-day global average solar flux at 10.7 cm normalized to 1 AU ( $\bar{F}_{10.7}$ ). The units are  $10^{-22} \text{ W m}^{-2} \text{ Hz}^{-1}$ . Dotted horizontal lines express the difference between the two last solar cycle minima. The seasonal and geomagnetic activity effects are removed from the data (after Emmert et al., 2010).

gives rise to the  $4.3 \mu\text{m}$  atmospheric emission; which results in achieving a more accurate knowledge of the  $\text{CO}_2$  non-LTE processes (see below). Also, the wide spectral range of MIPAS allow us to have simultaneous measurements of other atmospheric parameters, as the kinetic temperature (up to  $\sim 100$  km) from the  $\text{CO}_2$   $15 \mu\text{m}$  region, the thermospheric temperature from the  $\text{NO}$   $5.3 \mu\text{m}$ , and the  $\text{O}_3$  measurements (up to  $\sim 100$  km, that provides very accurate  $\text{O}(^1D)$  concentrations). The latter two facts lead both to a very accurate retrieval of the  $\text{CO}_2$  abundance from MIPAS spectra. Additionally, since MIPAS has a high sensitivity, it is able to measure the  $\text{CO}_2$  atmospheric emission in a wide altitude range, up to  $\sim 150$  km.

Thus, the major aim of this work is to retrieve global distributions of  $\text{CO}_2$  vmr profiles from MIPAS high resolution infrared spectra in the mesosphere and thermosphere (60-140 km).

The lack of knowledge of the non-LTE populations of the  $\text{CO}_2$  states emitting near  $4.3 \mu\text{m}$  is a limitation for the accurate retrieval of  $\text{CO}_2$  abundances from this emission, particularly from limb measurements (López-Puertas and Taylor, 2001; Kaufmann et al., 2002; Rezac et al., 2015). Non-LTE emissions are also affecting the temperature sounding from nadir  $4.3 \mu\text{m}$  spectral measurements. Thus, DeSouza-Machado et al. (2007) found a brightness temperature 10 K larger if they do not include non-LTE in the simulations of the Atmospheric InfraRed Sounder (AIRS) daytime radiances. Chen

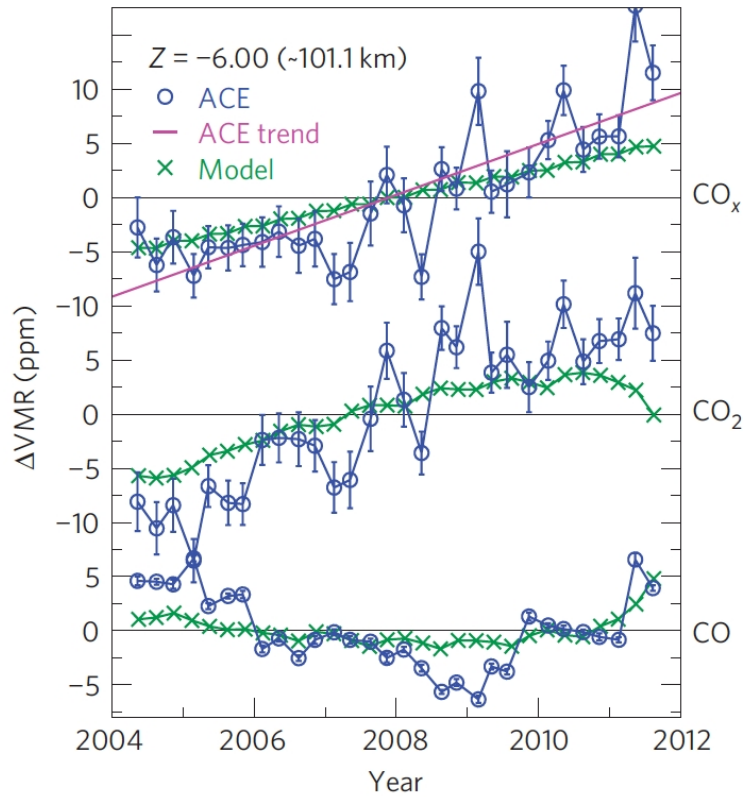


Figure 1.14: Residuals volume mixing ratios of  $\text{CO}_x$  (top),  $\text{CO}_2$  (middle) and  $\text{CO}$  (bottom). Results are shown after removal of seasonal-latitudinal effects at  $\sim 101$  km. ACE-FTS measurements are represented by blue circles and NCAR global mean model by green crosses. The linear trend is calculated from a linear least-squares fit of the ACE-FTS  $\text{CO}_x$  residuals (pink line). Errors bars are the estimated  $1\sigma$  uncertainty of the mean. (after Emmert et al., 2012)

et al. (2013) and Mengtao and Xiaolei (2015) have found similar results when analyzing the Infrared Atmospheric Sounding Interferometer (IASI) and the Cross-track Infrared Sounder (CrIS) measurements, respectively.

MIPAS spectra, however, with its high spectral resolution, offer an unprecedented information on the non-LTE emissions of the different  $\text{CO}_2$   $4.3 \mu\text{m}$  bands (fundamental, hot and isotopic) and on the processes populating its originating energy levels. Thus, the second major objective of this work is to derive new non-LTE collisional energy transfer rates between the different levels of  $\text{CO}_2$  emitting near 10, 4.3 and  $2.7 \mu\text{m}$  and with  $\text{N}_2$ . This information is necessary for performing the  $\text{CO}_2$  retrieval, therefore this objective was tackled first in thesis. The first direct consequence of this objective is that MIPAS  $\text{CO}_2$  abundances can be more accurate than those obtained before from previous limb emission instruments. Further, this non-LTE information is not only applicable to MIPAS but can also be used in other limb emission experiments like SABER, or the nadir emission instruments mentioned above.

The analysis of the  $4.3 \mu\text{m}$  emission spectra is very difficult because of the many lines of the many bands with so different optical thicknesses that conforms them.

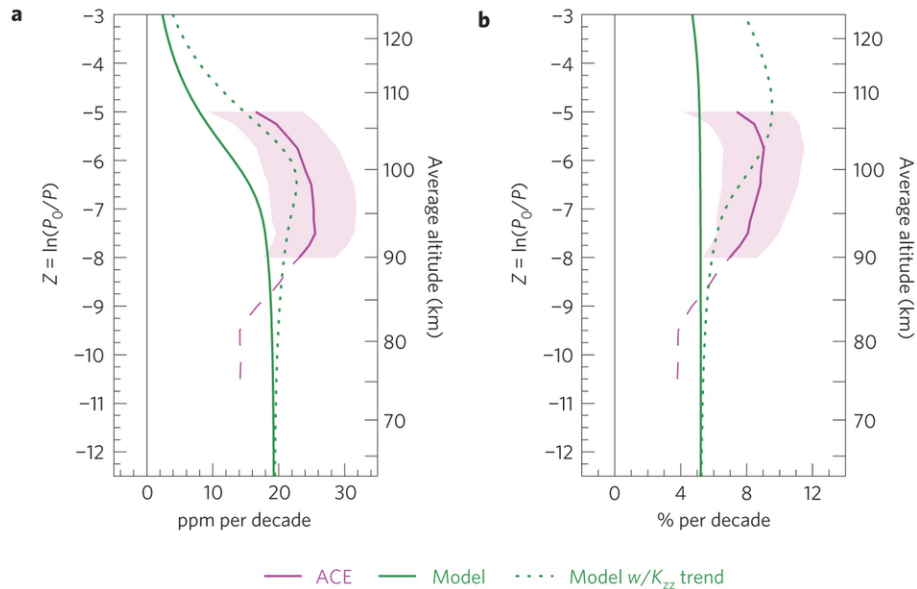


Figure 1.15: a) Absolute trends and b) relative trends of  $\text{CO}_x$  obtained by dividing the absolute trends by the profiles shown in Emmert et al. (2012) (Figure 4.1 therein). Pink lines represents ACE-FTS measurements, the solid green lines the NCAR global mean model and the dotted green, the global mean model with a 15% per decade eddy diffusion trend added.

Thus, to accomplish the second objective we have developed a non-LTE retrieval algorithm that retrieve the main non-LTE collisional parameters (the rate coefficients and their temperature dependence) from the MIPAS spectra in the 10 and 4.3  $\mu\text{m}$  regions. The  $\text{CO}_2$  vmr is jointly retrieved in this case in order to minimize the systematic errors. This algorithm is applied to a subset of the data, large enough and covering different atmospheric conditions, to obtain accurate rate coefficients. Once this is done, the non-LTE model is updated with the obtained collisional rates and then the retrieval of the  $\text{CO}_2$  vmr is performed. The inversion has been applied to two years of MIPAS data, 2010 and 2011.

As it is usual in these studies, the quality of the retrieved  $\text{CO}_2$  has been assessed, providing key parameters such as its noise errors and vertical resolution. A thorough analysis of the systematic errors of both the collisional rates and the retrieved  $\text{CO}_2$  vmr has also been performed.

In addition, we have carried out a validation study by comparing the MIPAS  $\text{CO}_2$  data with the previous independent measurements of ACE and SABER.

Furthermore the main physical features of the retrieved global distribution of  $\text{CO}_2$  have been analyzed with the help of the 3D Whole Atmosphere Community Climate Model (WACCM).

The  $\text{CO}_2$  data obtained in this work have been added to the MIPAS IMK<sup>10</sup>-IAA<sup>11</sup> database, for its use by the scientific community.

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## Chapter 2

# The MIPAS instrument

### *Abstract*

In this chapter we present a detailed description of the MIPAS instrument, its modes of operation, and the major characteristics of its measurements. First we explain the main characteristics of the ESA/Envisat mission and the importance of MIPAS measurements for the atmospheric science. Then, we described the scientific goals, from weather forecasting to upper atmospheric studies. Later, we describe the MIPAS design, its performance, and the different processing levels (0, 1b and 2) and the calibration of level 1b spectra. Then we outline the MIPAS spectral channels (A, AB, B, C and D) covering from 685 to 2410  $\text{cm}^{-1}$ . MIPAS was designed and operated to have a global latitudinal, longitudinal and vertical coverage. Thus, we also describe the different MIPAS observation modes. MIPAS was launched in March 1 2002 and was working until March 2004 in its so-called full spectral resolution mode. After January 2005, it was working in the reduced (also called "optimized" resolution mode. The MIPAS measurements analyzed in this work were taken during the period of reduced resolution. We finalize the chapter we a detailed description of the MIPAS observation modes.

### 2.1. Major Features

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a infrared Fourier transform spectrometer designed to measure limb atmospheric emission from the upper troposphere to the thermosphere in the mid-infrared (Fischer *et al.*, 2008). MIPAS was part of Envisat (ENViromental SATellite, see Figure 2.1), successfully launched on March 1<sup>st</sup>, 2002 aboard an Ariane 5 from the Guiana Space Center in Kourou, French Guiana. The spacecraft was placed into an helio-synchronous polar orbit with an inclination of 98.55° at a height of 860 km. Envisat, the largest Earth-Observation spacecraft ever built, was the first ESA (European Space Agency<sup>1</sup>) satellite dedicated to the Earth's observation. Its measurements comprises many different areas like the atmosphere, the oceans and its biology, or ice sheet.

Besides MIPAS there were another two instruments embarked on Envisat to study the Earth's atmosphere: the Global Ozone Monitoring by occultation of Stars (GO-

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<sup>1</sup>Envisat web site: <https://earth.esa.int/web/guest/missions/esa-operational-ee-missions/Envisat>



MOS) (Kyrölä et al., 2004) and the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) (Bovensmann et al., 1999). The three instruments were part of the Envisat Atmospheric-Chemistry section. The rest of the instruments on board Envisat were: An Advanced Synthetic Aperture Radar (ASAR), MEdium Resolution Imaging Spectrometer (MERIS), Advanced Along Track Scanning Radiometer (AATSR), Radar Altimeter 2 (RA-2), a microwave radiometer (MWR), Doppler Orbitography and Radio-positioning Integrated by Satellite (DORIS) and Laser Retro-Reflector (LRR) (see Figure 2.1).

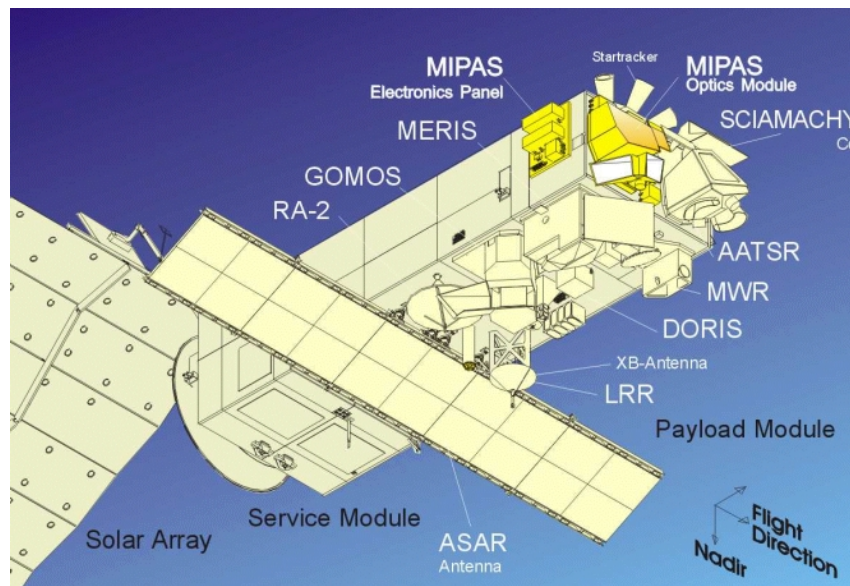


Figure 2.1: Envisat drawing showing its different parts. The ten instruments are pointed specifying their location on the satellite body. In the lower left corner nadir and flight direction are indicated. In yellow, MIPAS electronic panel and optics module are highlighted.

MIPAS has three main characteristics of special interest for non-LTE atmospheric radiance studies: i) a wide spectral coverage comprising the most important mid-IR atmospheric bands; ii) a high spectral resolution, able to resolve the ro-vibrational lines and; iii) its high sensitivity. In addition, MIPAS was operated at high spatial coverage and was measuring during 10 years, thus allowing to perform seasonal and mid-term studies. The instrument was designed using the knowledge gained by its predecessor, the MIPAS-b (atmospheric balloon).

## 2.2. Scientific Goals

MIPAS was conceived as an instrument able to study the dynamics and the chemistry of the upper troposphere, stratosphere, mesosphere and lower thermosphere. Furthermore the instrument should take measurements over a long period to address



climatological studies. The main scientific goals of the MIPAS project are:

- *The ozone chemistry and the stratospheric dynamics.* Including the ozone and CFC's monitoring, the Antarctic vortex, and the physical structure of the non-polar stratosphere.
- *The stratosphere-troposphere interaction.* Including the stratospheric waves propagation affecting the tropospheric weather, the tropical pipe and the tropospheric-stratospheric exchanges along the tropopause.
- *The physics and chemistry of the upper atmosphere.* Including the thermal structure, the energy balance, the chemistry and the dynamics. For that purpose parameters like temperature or trace gases concentrations such as H<sub>2</sub>O, O<sub>3</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> and NO were measured.
- *Climate and weather forecast.* MIPAS contributed in this sense with a decade of measurements of temperature and water vapor in the upper troposphere and stratosphere.

## 2.3. Design

To achieve the above-mentioned scientific requires an instrument with high spectral resolution in the mid-IR combined with a wide spectral coverage and high sensitivity. For this reason, ESA selected as the core instrument of the atmospheric package, an IR Fourier transform spectrometer (FTIR), i.e., MIPAS.

The main advantages of FTIR instruments for taking atmospheric measurements are:

- FTIR instruments are able to measure signal independently of sunlight conditions. This is because the Planck function peaks near 10  $\mu\text{m}$  at typical atmospheric temperatures, i.e. atmospheric signal is higher in the infrared.
- The mid-infrared region allows smaller instruments than those measuring at longer wavelengths. This is determined by the diffraction limits and the higher spectral resolution.
- The instruments operating in the mid-infrared region can be calibrated by observing cold space and black bodies.

On the other hand, the FTIR mechanical complexity is the main disadvantage. A very high precision alignment is needed and the different optic elements should have space for motion and stability. Another problem is the optics cooling (down to 210 K) which is used to reduce its background thermal emission. Thus building an instrument with these special characteristics for space, has additional technical difficulties.

MIPAS was a complex instrument made of several sub-systems. Its optical module was located at the opposite part to the solar light of Envisat and consisted of three main parts: the Front-End optics, the interferometer and the focal planes subsystem (see Figure 2.2).

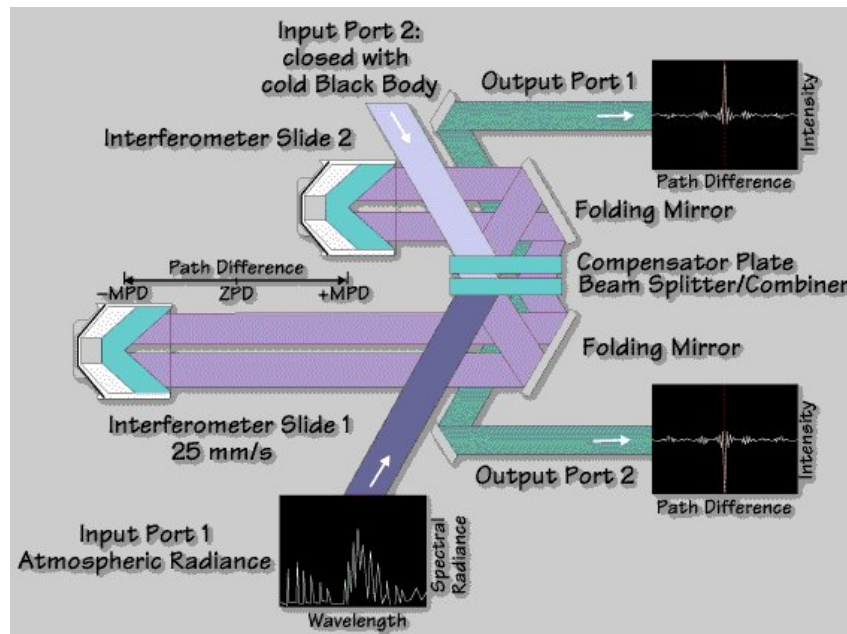


Figure 2.2: The MIPAS optical system formed by the Front-End optics (lower part), the interferometer (upper right) and the focal planes subsystem (upper right).

The limb atmospheric radiation entered through the frontal part. Then it was reflected in an azimuthal mirror first and then in an elevation mirror. MIPAS was able to select the orientation and the altitude of the target by using these two mirrors. Later, the radiation passed through a collimator telescope that fit the beam size in accordance to the size of the interferometer aperture. When the radiation entered into the Michelson interferometer, the beam was split in two. Then the beams were directed into two moving mirrors which redirected them into the beam recombiner. The recombined radiation emerging from the interferometer formed the interference pattern. At this point the beam was again split into two beams redirected into the two output ports. Finally the radiation beams passed through to the focal planes subsystem where each beam was separated in spectral channels by optical filters. In order to increase the sensitivity, the beams were directed onto CMT (Cadmium Mercuride Telluride) detectors. These detectors were cooled to 70 K in order to reduce the thermal emission and to minimize its own noise. As we will see later, MIPAS was designed to cover from 4.15 up to 14.6  $\mu\text{m}$  (685 to 2410  $\text{cm}^{-1}$ ) using five spectral channels. The separation of the beam into five spectral regions was done in order to reduce the noise arising from detectors and to ease the temperature measurements.

As we have seen above, the MIPAS output signal is an interferogram formed

from the two beams combined at the Michelson interferometer. In an interferogram we find a number of dark and bright lines composing the interference pattern. The dark lines, where the intensity is zero, derives from the *destructive interference* of the two beams. The bright ones or zones of maximum intensity, comes from the *constructive interference*. The aspect of the pattern is defined by the distance between the two mirrors, i.e. the optical path, and the wavelength of the incoming beam of light. The radiance information is given by the intensity of the output function. When a Fourier Transform is applied on an interferogram, the function is decomposed into the frequencies that make it up, thus obtaining the frequency spectrum.

The MIPAS spectral resolution is given by the optical path difference (OPD<sup>2</sup>) between the mirrors. As we will describe later in Section 2.5, a mechanical failure in March 2004 forced to reduce the OPD in about half of its length and thus decreasing the spectral resolution in the same quantity. Nevertheless, MIPAS spectral resolution was still very high and also allowed to gain in spatial resolution since the integration time of the interferometer sweep was reduced and allowed a better vertical and horizontal sampling.

## 2.4. Calibration and Characterization

The raw data (interferograms) obtained from MIPAS are not adequate to be directly used in scientific studies. Thus it is necessary to transform the interferograms into radiometrically and spectrally calibrated and geo-located spectra by applying a series of specific procedures (see Fig. 2.3).

In a first step, the interferogram was pre-processed aboard Envisat producing the *level 0* data. This procedure includes amplification, complex filtering, compression and digitalization<sup>3</sup> of the signal. The goal of all this processing was to reduce the instrument data rate to less than 550 kbits/s. Later, the data set, information about telemetry and auxiliary data for calibration was sent to ESA ground station. Then the data processing was divided into two phases: *level 1b* and *level 2*. In the *level 1b* processing, the Fast Fourier Transform (FFT) is applied and the raw interferogram is converted into a calibrated spectra. In the following, we describe the major steps of the *level 1b* data processing.

- *Radiometric calibration.* This is divided in two steps, offset and gain calibration. Regularly calibrations were carried out in order to assign absolute radiance units to the measured spectra. The offset calibration was taken from the thermal emission of the instrument obtained by pointing it to the deep space, where the 3 K background emission was measured (and actually considered negligible). The gain calibration was obtained from the spectra radiance from a black body at a known temperature ( $L_{BB}$ ). From the difference of the measured spectra from the blackbody and from the deep space spectra,  $S_{BB}$  and  $S_{DS}$  respectively,

<sup>2</sup>The spectral resolution is about 0.6/OPD

<sup>3</sup>By the on board analogue-to-digital converter (ADC)

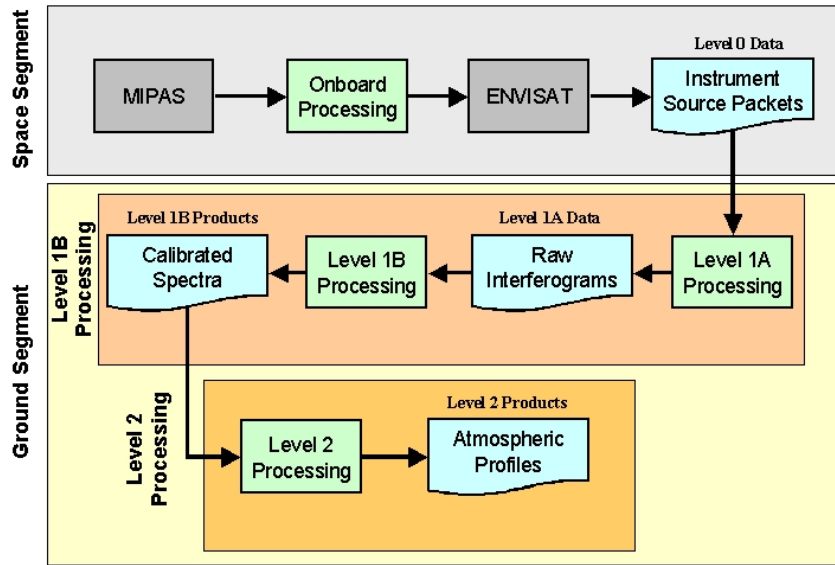


Figure 2.3: Scheme of the different parts of MIPAS data processing. The *level 0*, *level 1b* and *level 2* are briefly described.

the gain function is obtained as follows,

$$G = \frac{L_{BB}}{S_{BB} - S_{DS}}. \quad (2.1)$$

The calibration of the spectra is obtained by using the following equation,

$$L_{atm} = G(S_{atm} - S_{DS}), \quad (2.2)$$

where  $S_{atm}$  is the measured spectra and  $L_{atm}$  the calibrated spectra. The gain calibration could be affected by the ice formation on the cooled detector optical components. The stability of the gain calibration allowed to perform it once per week.

Regarding offset calibrations, much less stable, they were performed each  $\sim 7$  minutes. During these calibrations the interferogram was cleaned of spurious spikes due to cosmic rays. The difference of sampling between measured and calibrated interferograms were also corrected. The imaginary component of  $L_{atm}$ , which should only contain noise, was used for quality verification and for computing the noise equivalent spectral radiance of the measurement.

- *Noise Equivalent Spectral Radiance (NESR).* The noise levels were obtained from the data. Depending on the spectral channel it ranges from 3 to 50  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ . The NESR within the 5 spectral channels did not show a significant systematic drift over the time. In addition, the ice accumulation on the detectors could degrade the NESR up to 20% with respect to regular ice free conditions.
- *Non-linearity of the detector.* The amount of incident photons could affect to

the linearity of channels A, AB and B. This fact could trigger important errors in radiometric calibration so it was previously corrected. The interferogram was scaled using the following polynomial function

$$k = 1 + d_0F + d_1F^2 + d_2F^3 + d_3F^4, \quad (2.3)$$

where  $k$  is the black body emission at a given temperature,  $F$  is the total flux incident on the detector and  $d_i$  are the non-linearity coefficients for each detector. The non-linear behavior of the detector was characterized on board, within the device, and in the ground station simultaneously.<sup>4</sup>

- *Spectral calibration.* The Doppler effect due to the orbital movement of the satellite with respect to the atmosphere was corrected. As usual, reference lines with well known frequencies were chosen. For MIPAS, one line per channel was chosen: two ozone lines ( $802.5074 \text{ cm}^{-1}$  and  $1125.2085 \text{ cm}^{-1}$ ) and three water vapor lines ( $1409.9686 \text{ cm}^{-1}$ ,  $1672.4750 \text{ cm}^{-1}$  and  $1966.2615 \text{ cm}^{-1}$ ). In order to assure the stability of the calibration, it was performed every four limb scans.
- *Instrument line shape (ILS) calibration.* The output radiance measured by a given instrument is the response of the device to the input radiance coming from the atmosphere. The different elements of the instrument distort the incoming radiance. In an ideal case, the instrument response to a monochromatic source is a *sync* function (see Figure 2.4).

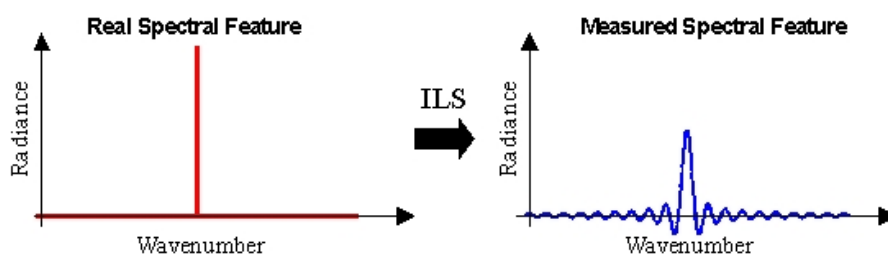


Figure 2.4: Interferometer's response to an ideal spectral line. Left panel (red line) shows an input monochromatic atmospheric radiance. Right panel (blue line) shows the response of the instrument, a *sync* function, i.e. the convolution of the input radiance with the instrument line shape (ILS).

Thus, the measured spectrum is the convolution of an atmospheric spectrum with the ILS. The full width at half maximum of the ILS main lobe gives the spectral resolution. The secondary minor lobes affect the measured spectrum in a broader spectral interval. They can be reduced by a smooth truncation of the interferogram close to the maximum OPD (apodization). In this way a convolution of the ILS with an apodization function (the AILS) is needed

<sup>4</sup>A new non-linearity correction has been recently derived (Manfred Birk and Georg Wagner, TN: Radiometric impact of new non-linearity analysis, 12 Nov. 2013). This has been applied to the newest V7 L1b data. However, this most recent version of L1B is not used in this work.

before convolving the measured spectrum. The adjustments of MIPAS ILS were performed using a physical model of the interferometer.

- *Line of sight calibration.* This is required to determine pointing biases and harmonic variations. It is based on observations of stars moving through the field of view of the instrument at the short wavelength channels. The calibration gives a pointing correction derived from variations between the Envisat pointing system and the line of sight of MIPAS.<sup>5</sup>
- *Field of View (FOV) modeling.* The characterization of the FOV was performed before and after the launch. Pre-launch FOV width was fixed in 52 mdeg (FWHM) in the elevation direction. After the launch, the FOV width was confirmed to be better than 1.3 mdeg in the elevation direction.

Level 2 MIPAS data are the retrievals of the geophysical parameters obtained from level 1b calibrated data. To perform retrievals is necessary to dispose of a forward radiative transfer code used for the simulations of the measured spectra. In the case of non-LTE conditions measurements, a modeling of the non-LTE populations is also needed.

## 2.5. Spectral Coverage and Resolution

MIPAS covers the spectral range from 4.15 up to 14.6  $\mu\text{m}$  (685 to 2410  $\text{cm}^{-1}$ ) divided into five channels or bands: *A*, *AB*, *B*, *C* and *D*. This configuration optimized the sensitivity of each channel. As we show in Fig. 2.5, MIPAS is able to measure a large number of atmospheric constituents, including pressure (LOS) and temperature from the  $\text{CO}_2$  15  $\mu\text{m}$  bands,  $\text{O}_3$ , practically all species controlling the  $\text{O}_3$  chemistry, water vapor, the six species comprising  $\text{NO}_y$ , several tracers ( $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{CO}$ ), the  $\text{CO}_x$  ( $\text{CO}+\text{CO}_2$ ) budget, many tropospheric contaminants (PAN, HCN, etc.), bromine nitrate ( $\text{BrONO}_2$ ), PSCs, aerosols, among others. In addition, MIPAS also measure the 4.3  $\mu\text{m}$  emission from  $\text{CO}_2$  in band D, not exploited operationally, but that allow to retrieve the  $\text{CO}_2$  abundance in the middle and upper atmosphere, the subject of this work. We detail below the spectral channels of MIPAS and the main species that can be retrieved from them.

- *Channel A:* From 685 to 970  $\text{cm}^{-1}$  with a NESR of 30  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ . Measurable species:  $\text{CO}_2$ ,  $\text{O}_3$ , CFC's,  $\text{HNO}_3$ ,  $\text{ClONO}_2$ ,  $\text{HNO}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{OCS}$ ,  $\text{SF}_6$  and aerosols.
- *Channel AB:* From 1020 to 1170  $\text{cm}^{-1}$  with a NESR of 24  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ . Measurable species:  $\text{O}_3$ ,  $\text{N}_2\text{O}$ , CFC12 and aerosols.
- *Channel B:* From 1215 to 1500  $\text{cm}^{-1}$  with a NESR of 12  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ . Measurable species:  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{ClONO}_2$ ,  $\text{CF}_4$ ,  $\text{COF}_2$  and HCN.

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<sup>5</sup>We should mention that the LOS is more accurately retrieved later, in the processing of L2.

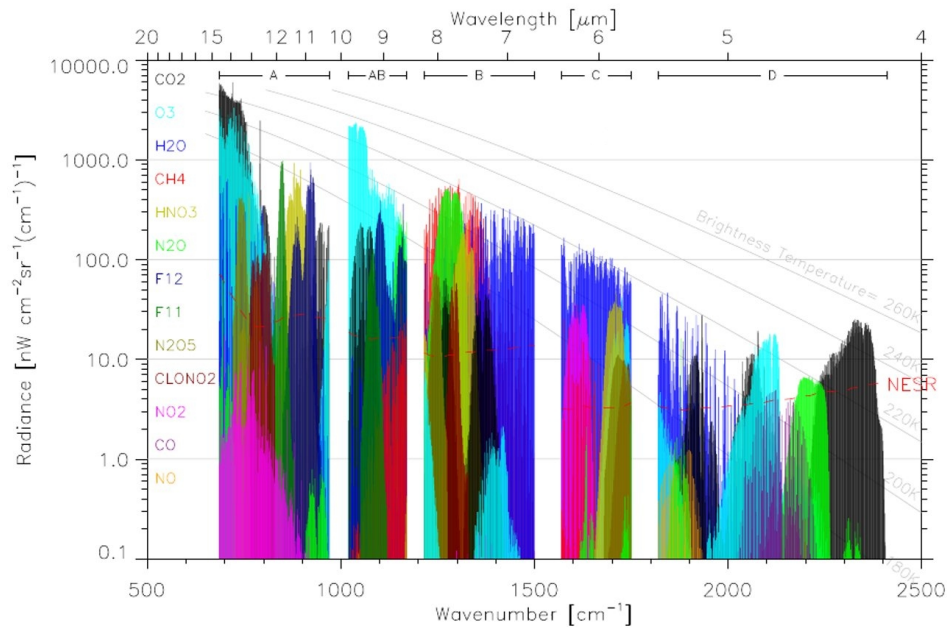


Figure 2.5: Simulations of the spectral contributions of different atmospheric gases at a tangent height of 12 km for the five MIPAS channels. The red dashed line represents the noise equivalent spectral radiance (NESR).

- *Channel C*: From 1570 to 1750  $\text{cm}^{-1}$  with a NESR of 4  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ . Measurable species:  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{O}_3$ , and  $\text{HNO}_3$ .
- *Channel D*: From 1820 to 2410  $\text{cm}^{-1}$  with a NESR of 4  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ . Measurable species:  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{OH}$ ,  $\text{NO}^+$ ,  $\text{H}_2\text{O}$ ,  $\text{OCS}$  and  $\text{COF}_2$ .

The original spectral resolution of MIPAS, known as full resolution (FR), was of  $0.025 \text{ cm}^{-1}$  that was operating from September 2002 to March 2004. Due to a malfunction of the mirrors movements, the optical pathway was reduced from 20 to 8 cm, leading to a reduction in the spectral resolution of 41%, i.e. to  $0.0625 \text{ cm}^{-1}$  (optimized spectral resolution, OR). The OR was introduced in January 2005 and was operating until the end of Envisat mission in April, 2012. All the data used in this work were taken with the optimized spectral resolution.

## 2.6. Spatial and Temporal Coverage

The spatial and temporal coverage of MIPAS are defined by its instrumental characteristics, its mode of operation (Fig. 2.6) and the Envisat orbit. MIPAS was operated in various modes of limb measurements, sampling different tangent heights<sup>6</sup> intervals. The targeting of a given tangent height was carried out by using the elevation mirror. MIPAS kept the TH stable while the interferogram sweep was

<sup>6</sup>Tangent Height (TH): the lowest height pointed by the line of sight.



Table 2.1: MIPAS filters. The spectral range (in  $\text{cm}^{-1}$ ), the average noise (in  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ ) and the most important absorbing or emitting species are specified for each filter.

Band	Spectral range	NESR	Species
A	685 – 970	30	$\text{CO}_2$ , $\text{O}_3$ , CFCs, $\text{HNO}_3$ $\text{ClONO}_2$ , $\text{HNO}_4$ , $\text{C}_2\text{H}_2$ , $\text{C}_2\text{H}_6$ $\text{CCl}_4$ , OCS, $\text{SF}_6$ , aerosols
AB	1020 – 1170	24	$\text{O}_3$ , $\text{N}_2\text{O}$ , CFC12, aerosols
B	1215 – 1500	12	$\text{N}_2\text{O}$ , $\text{H}_2\text{O}$ , $\text{CH}_4$ , $\text{HNO}_3$ , $\text{N}_2\text{O}_5$ $\text{ClONO}_2$ , $\text{CF}_4$ , $\text{COF}_2$ , HCN
C	1570 – 1750	4	$\text{H}_2\text{O}$ , $\text{NO}_2$ , $\text{O}_3$ , $\text{HNO}_3$
D	1820 – 2410	4	$\text{CO}_2$ , CO, NO, $\text{O}_3$ , $\text{N}_2\text{O}$ , OH, $\text{NO}^+$ $\text{H}_2\text{O}$ , OCS, $\text{COF}_2$

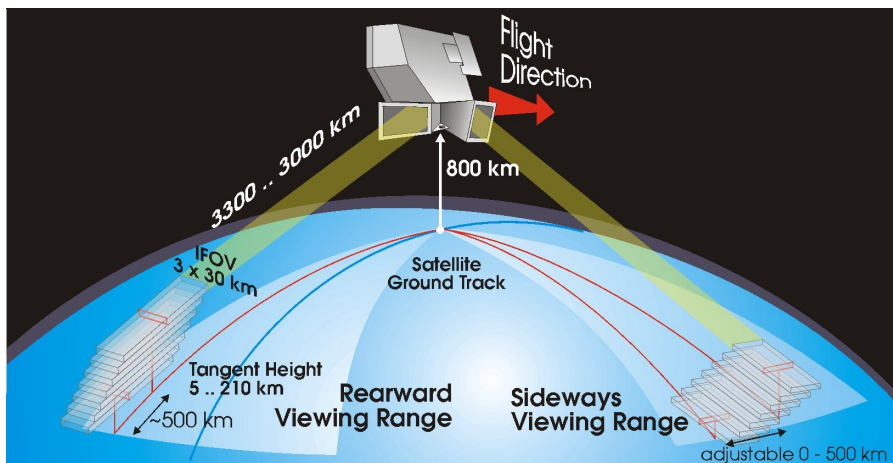


Figure 2.6: Observational strategy of MIPAS.

acquired. This time was of 4.45 s for the full resolution spectral mode and 2.1 s for the optimized resolution spectra. Later, discrete jumps were performed pointing at different TH's to finally obtain a limb scan sequence. Each sequence of sweeps, i.e., the whole scan, was started always at the uppermost tangent height and moving downwards to maximize the horizontal resolution (see Table 2.2). MIPAS observed in rearward direction taking pole to pole measurements as Envisat moves in its polar orbit. MIPAS was also designed to take sideways (cross track) scans. The original idea was to be used for monitoring volcanic eruptions, measure across the terminators and other scientific topics (Laurentis, 2005; Oelhaf, 2008). However, along the MIPAS lifetime, this mode was very scarcely used.

In general, MIPAS was designed to observe from 5 to 170 km in altitude (with steps from 1 to 8 km). The field of view of MIPAS is 30 km in the horizontal direction



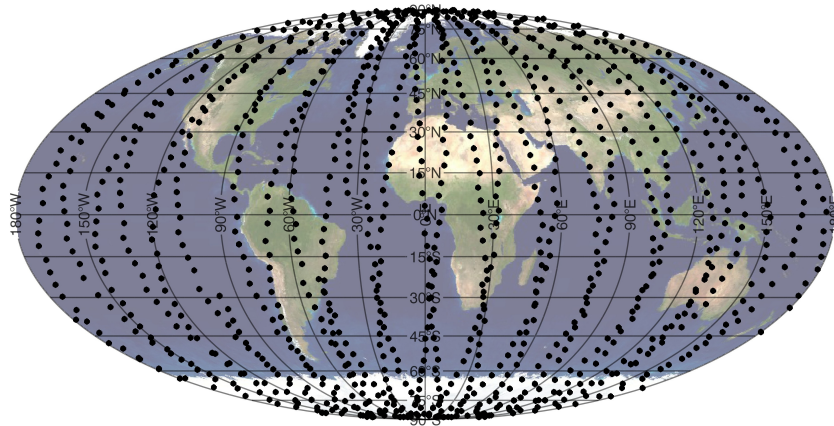


Figure 2.7: MIPAS Upper Atmosphere (UA) mode spatial coverage for a single day (January 17, 2010). Each dot stands for a single scan.

and 0.9 mrad in the vertical. Thus, the spatial vertical sampling is  $\sim 3$  km in the TH point. The atmospheric path along the line of sight is typically 400 km and the horizontal spacing between profile single measurements depended on the observation mode (ranging from 200 to 500 km).

With its helio-synchronous orbit, Envisat spent 100.6 min per orbit, about 14 orbits per day. As mentioned above, the time for taking an optimized resolution spectra is 2.1 s, this translates into more than 1000 scans per day in Upper Atmosphere mode. The near-polar orbit of Envisat and MIPAS lifetime of 10 years allowed to measure the temperature and species abundances for time scales of days, months, seasons and years. Times scales of hours, however, were hardly resolved since MIPAS took only 2 local time of measurements, 10 am and 10 pm.

Driven by the scientific studies, different observations modes were devised attending to: i) its vertical coverage; ii) its vertical sampling, and iii) its horizontal resolution. Since degraded spectral resolution was implemented in 2005, new observation modes for faster soundings were defined. The data analyzed in this work corresponds to the OR (or phase 2) period. Hence we describe here only the observations modes of this period (see Table 2.2).

- *Nominal (NOM - RR Nominal Mode)*. Designed to cover the upper troposphere, the stratosphere and the lower mesosphere. NOM was devised to study the stratospheric dynamics and ( $O_3$ ) chemistry, to provide climatological data and to carry out trend analysis. The vertical coverage ranges from 7 to 72 km. MIPAS performs 27 sweeps, at tangent heights steps of 1.5 km in the upper troposphere/lower stratosphere (UTLS) to 4 km steps at the highest altitudes. The spatial displacement (horizontal sampling) of this mode is 410 km. The time to take the whole scan is of 56.7 s.
- *Upper Troposphere Lower Stratosphere (UTLS)*. This mode covers tangent altitudes from 5.5 up to 49 km with an horizontal displacement of 290 km and

Table 2.2: MIPAS observations modes for the optimized resolution phase of operation. It lists the sweep number and the tangent heights of the limb scan sequence for each observation mode.

Sweep	Nominal	UTLS-1	UTLS-2	MA	UA	NLC	AE
#1	72	49	42	102	172	102	38
#2	67.5	44.5	37	99	167	99	35
#3	63	40	33	96	162	96	29
#4	59	35.5	29	93	157	93	24.5
#5	55	31	26	90	152	90	20
#6	51	28	23	87	147	87	17
#7	47	25	20	84	142	85.5	15
#8	44	23	18	81	137	84	13
#9	41	21	16	78	132	82.5	11.5
#10	38	19	14	75	127	81	10
#11	35	17.5	12	72	122	79.5	8.5
#12	32	16	–	69	117	78	7
#13	30	14.5	–	66	112	75	–
#14	28	13	–	63	107	72	–
#15	26	11.5	–	60	102	69	–
#16	24	10	–	57	99	66	–
#17	22	8.5	–	54	96	63	–
#18	20.5	7	–	51	93	60	–
#19	19	5.5	–	48	90	57	–
#20	17.5	–	–	45	87	54	–
#21	16	–	–	42	84	51	–
#22	14.5	–	–	39	81	48	–
#23	13	–	–	36	78	45	–
#24	11.5	–	–	33	75	42	–
#25	11.5	–	–	30	72	39	–
#26	8.5	–	–	27	69	–	–
#27	7	–	–	24	66	–	–
#28	–	–	–	21	63	–	–
#29	–	–	–	18	60	–	–
#30	–	–	–	–	57	–	–
#31	–	–	–	–	54	–	–
#32	–	–	–	–	51	–	–
#33	–	–	–	–	48	–	–
#34	–	–	–	–	45	–	–
#35	–	–	–	–	42	–	–
<b>Total</b>	<b>27</b>	<b>19</b>	<b>11</b>	<b>29</b>	<b>35</b>	<b>25</b>	<b>12</b>

performing 19 sweeps. The vertical sampling is 1.5 km in the lowest region and 4 km in the upper region, similar to the nominal mode. There is a variant of the

UTLS mode, the UTLS-2, designed to test bi-dimensional retrievals. UTLS-2 carried out 11 sweeps with a horizontal displacement of 180 km in a time of 23.1 s and with a vertical coverage from 12 up to 42 km.

- *Middle Atmosphere (MA)*. This mode covers part of the stratosphere, the mesosphere, and the lower thermosphere. This observation mode is used to study the middle atmosphere and its interaction with the lower atmosphere. The vertical coverage is from 18 up to 102 km with 29 sweeps (60.9 s) equally spaced by 3 km and with an horizontal displacement of 430 km.
- *Upper Atmosphere (UA)*. This mode is principally dedicated to study the thermosphere, mainly the temperature and the NO abundance. It covers from 42 to 172 km using 35 sweeps in 73.5 s. In the 42 to 102 km interval the vertical sampling is equally spaced at 3 km and in the upper region is 5 km. The horizontal displacement is of 515 km.
- *Noctilucent Clouds (NLC)*. This mode is similar to the UA mode but truncated at 102 km altitude. Additional heights are included at 79.5, 82.5 and 85.5 km, in order to get a better vertical resolution and easy the study of the noctilucent clouds. This mode is used regularly in the mentioned regions during polar summer conditions in both hemispheres. MIPAS takes the whole scan in 52.5 s.
- *Aircraft Emission (AE)*. This mode was designed to try to detect aircraft emission of gases and how can they affect the chemistry of the upper troposphere and the lower stratosphere. Using this mode MIPAS scan for 12 sweeps (25.2 s) with a vertical coverage from 7 to 38 km.

As we mentioned before, the first measurements of MIPAS were taken in March 2002. The instrument continued working almost uninterruptedly from September 2002 until April 2004 using the full resolution (FR) mode. Since January 2005 MIPAS was operated in the optimized resolution mode (OR). However MIPAS was not working on a 100% duty cycle until mid-2007. From this date until April 2012 the nominal mode were used a 80% of the total time; the middle atmosphere and upper atmosphere modes were used one day in ten; the NLC mode were used three days after each solstice in each hemisphere; and the remaining modes were used only occasionally. The MIPAS observations finished on 8 April 2012 when Envisat passed through a communications anomaly. The end of the Envisat mission was announced by ESA on 9 May 2012. Nowadays the satellite is drifting at an altitude of 790 km as a part of the space debris orbiting planet Earth.

## 2.7. MIPAS Data Used in this Work

In this work we analysed the MIPAS upper atmosphere (UA) observation mode. This mode has the most extended altitude coverage (50 to 172 km) allowing to retrieve CO<sub>2</sub> in the highest possible altitude range. Also, MIPAS single spectra taken during daytime in the region of the CO<sub>2</sub> 4.3 μm emission have a good signal to noise ratio

up to about 140 km tangent height. Since several bands of CO<sub>2</sub> are optically thick in the limb up to tangent altitudes as high as 100-110 km, it was then very important to have measurements above that altitude, i.e. to use the UA instead of the MA mode, to constrain the upper atmospheric emissions in the retrieval of CO<sub>2</sub>. As mentioned before, MIPAS took UA spectra in the period of mid-2007 until March 2012. The concrete days of measurements are listed in Table 2.3. For performing the retrieval we used the geo-located and calibrated MIPAS *level 1b* Version V5 (5.02/5.06) spectra provided by ESA (Perron et al., 2010; Raspollini et al., 2010).

The level 2 dataset is obtained by the IMK/IAA retrieval processor which includes the forward model Karlsruhe Optimized and Precise Radiative transfer Algorithm (KO-PRA) and the non-LTE model Generic Radiative traNsfer AnD non-LTE population Algorithm (GRANADA), both further explained in Chapter 4.

Table 2.3: MIPAS observations days in the upper atmosphere (UA) mode.

	2007	2008	2009	2010	2011	2012	#Days
January	–	9, 17, 27	2, 12, 19, 20	9, 17	4, 14, 24, 30, 31	9, 24, 26, 28, 30	19
February	–	6, 16, 26	6, 16, 26	18, 28	1, 13, 23	1, 3, 5, 7, 18, 28	17
March	22	7, 17	8, 18, 28	10, 30	5, 15, 25	9, 19, 29	14
April	–	6, 16, 26	7, 17	9	14, 24	8	9
May	–	16, 26, 31	7, 17, 27	19, 29	4, 14	–	10
June	–	9, 22	6, 16, 26	8, 18, 28	3, 13, 23	–	11
July	–	16, 26	16, 26	18, 28	3, 14, 27	–	9
August	–	5, 15, 25	2, 12, 22	7, 17, 27	4, 12, 22	–	12
September	21,22,23	4, 14, 24	1, 11, 21	6, 16, 26	1, 11, 21	–	15
October	–	4, 14, 24	1, 11, 21	6	1, 11, 21, 31	–	11
November	5, 15, 25	3, 13, 23	30	5, 15, 25	10, 20, 30	–	13
December	10, 20, 30	3, 13, 23	10, 20, 30	5, 15, 25	20, 30	–	14
<b>#Days</b>	<b>10</b>	<b>33</b>	<b>33</b>	<b>27</b>	<b>36</b>	<b>15</b>	<b>154</b>

## Chapter 3

# Basic Theory of Atmospheric Radiative Transfer and the Inversion Problem

### *Abstract*

In this chapter we present the basic aspects of radiative transfer theory required for the understanding of this work. First we describe the basic steps to obtain the Radiative Transfer Equation (RTE), its formal solution, and its form for limb observations. In this part, the radiance ( $L_\nu$ ), the flux ( $F_\nu$ ), the heating rate ( $h_\nu$ ), the absorption/emission coefficients ( $k_\nu$  and  $j_\nu$ ) and the optical thickness ( $\tau_\nu$ ) are defined. Later we explain the main concept of Local Thermodynamic Equilibrium (LTE) which allows to express the source function  $J_\nu(T)$  by the Planck's function  $B_\nu(T)$ . LTE breakdown conditions and main considerations to obtain the non-LTE source function are further explained. For this purpose it is necessary to know all the microscopic processes populating the different excited levels and gather them into the Statistical Equilibrium Equation (SEE). The radiance emitted by an air parcel is calculated from the resolution of the coupled system of RTE and SEE equations. Then we describe the inverse problem, i.e., how obtain information on the different atmospheric parameters starting from the measured emission. Besides, we describe the jacobian matrix, the covariance matrix ( $S_y$ ), the treatment of *a priori* information including the regularization, and the Levenberg-Marquardt damping. All this information is required in the inversion process in order to retrieve atmospheric parameters. Finally, we present a brief description of the diagnostics, including the averaging kernel, the residuals, and the retrieval errors.

### 3.1. Introduction

Energy transfer in Earth's atmosphere occurs mainly in form of electromagnetic radiation. This physical phenomenon is known as the radiative transfer. Accordingly, to know the basics of the interaction between radiation and matter is essential to perform an appropriate analysis in this area. The main processes that characterize the interaction of the radiation with a given medium like the terrestrial atmosphere are: absorption, emission and scattering.

- *Absorption*: in this process the incident radiant energy is retained by the atmosphere. Considering the molecular scale, we define the absorption as the phenomenon of acquiring photons from incident radiation in order to populate its excited levels. Since absorption depends directly on the molecular density of the medium, absorption becomes stronger at lower atmospheric layers.
- *Emission*: the emission of a photon in a de-excitation process of atmospheric molecules.
- *Scattering*: the general physical process where a photon changes the direction of its propagation trajectory ( $\vec{s}$ ) by one or more non-uniformities located in the medium. In this way the light is deviated from its original optical path by the atmospheric molecules.

As we mention in the first chapter, CO<sub>2</sub> vibration-rotation transitions emit and absorb electromagnetic radiation principally in the infrared. Scattering has a strong dependence on the wavelength ( $\sim \lambda^{-4}$ ) and, since we study here only infrared emissions, we can neglect this effect in our analysis. The presence of clouds could require to deal with scattering (specially at near-infrared wavelengths) but they are mostly restricted to the lower atmosphere and do not affect the altitudes where non-LTE emissions prevails. Under certain conditions, i.e, during the polar summer, there can be found clouds in the upper mesosphere. They are so thin, however, that their effects, compared to the CO<sub>2</sub> absorption/emission at the IR wavelengths studied here, are negligible.

The incoming energy comes from solar radiation from above, and upwelling flux reaching the higher atmospheric layers from below. These photons interacts with the different layers of the atmosphere and also with the terrestrial surface<sup>1</sup>. Thus the amount of solar energy in interaction with the the different atmospheric layers and with the surface, are important drivers for the atmospheric thermal structure.

It is worth to highlight that knowledge of radiative transfer under non-LTE conditions is necessary for understanding the role of CO<sub>2</sub> emissions in the mesosphere and lower thermosphere.

## 3.2. Radiative Transfer

First we present the radiative transfer theory. The photons of all wavelengths travelling in all directions define the radiative field (Figure 3.1) at a given point P and can be described with the concept of radiance or specific intensity. The radiance,  $L_\nu$ , is related to the amount of energy,  $dE_\nu$ , within the frequency interval  $(\nu, \nu + d\nu)$ , transported by the radiative field across an infinitesimal area,  $d\sigma$  (centred at P), along a direction  $\mathbf{s}$  (forming an angle  $\theta$  with  $\mathbf{n}$ ) and confined at a solid angle  $d\omega$  during the

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<sup>1</sup>In this work we approximate the surface Earth's radiation as a black body radiation.

time  $dt$ , by

$$dE_\nu = L_\nu(P, \mathbf{s}) \cos \theta \, d\sigma \, d\omega \, d\nu \, dt. \quad (3.1)$$

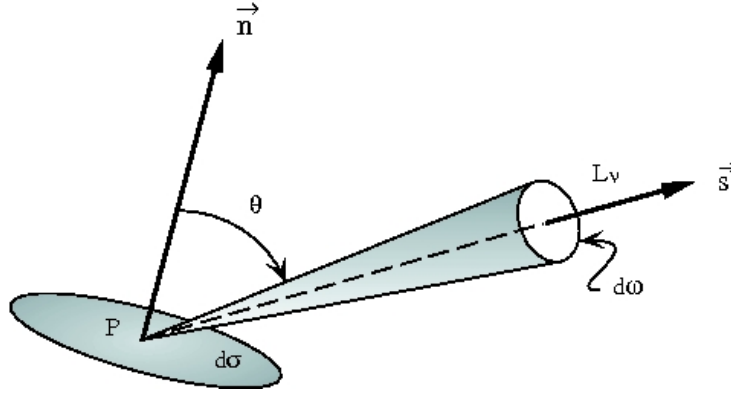


Figure 3.1: Basic radiance element and its elementary parts.

Integrating  $L_\nu(P, \mathbf{s})$  over the frequency interval we obtain the spectrally-integrated radiance,  $L(P, \mathbf{s})$ , with dimensions of  $\text{W m}^{-2} \text{sr}^{-1}$ . Integrating again over solid angle we obtain the flux density. If we integrate over all  $\mathbf{s}$  directions in  $d\omega$ , the radiative flux along the  $\mathbf{n}$ -direction is obtained:

$$F_{\nu, n}(P) = \int_{\omega} L_\nu(P, \mathbf{s}) \cos \theta \, d\omega. \quad (3.2)$$

For a three dimensional Cartesian coordinate system with the typical unit vectors ( $\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$ ), we can express the radiative flux in the vector Cartesian form:

$$\cos \theta = \mathbf{n} \cdot \mathbf{s} = (\mathbf{n} \cdot \mathbf{i})(\mathbf{s} \cdot \mathbf{i}) + (\mathbf{n} \cdot \mathbf{j})(\mathbf{s} \cdot \mathbf{j}) + (\mathbf{n} \cdot \mathbf{k})(\mathbf{s} \cdot \mathbf{k}), \quad (3.3)$$

$$F_{\nu, n}(P) = \int_{\omega} L_\nu(P, \mathbf{s}) (\mathbf{n} \cdot \mathbf{s}) \, d\omega, \quad (3.4)$$

$$\mathbf{F}_\nu(P) = F_{\nu, x}(P) \mathbf{i} + F_{\nu, y}(P) \mathbf{j} + F_{\nu, z}(P) \mathbf{k}. \quad (3.5)$$

The divergence of the radiative flux expresses the net rate at which the energy per unit volume of the radiation field is increased or decreased. This magnitude is represented by the scalar quantity  $h_\nu$  known as the heating/cooling rate (hereafter heating rate):

$$h_\nu = -\nabla \cdot \mathbf{F}_\nu(P) = \int_{\omega} \frac{dL_\nu}{ds} \, d\omega. \quad (3.6)$$

Once we have defined these basic quantities we can construct of the Radiative Transport Equation (RTE). First we express the variation of radiance traveling through a path  $ds$ . The form of the equation including only extinction, either absorption or scattering, is given by the Lambert's law:

$$dL_\nu = -e_\nu n_a L_\nu ds \Rightarrow dL_\nu = -k_\nu n_a L_\nu ds. \quad (3.7)$$

In this equation we include the number density<sup>2</sup>,  $n_a$ , of the absorbing molecules, the atmospheric extinction coefficient,  $e_\nu$ , for absorption and scattering; and the radiance,  $L_\nu$ . Neglecting the scattering we consider the absorption coefficient,  $e_\nu = k_\nu$ .

Taking into account only the increase of the radiance when traveling along the path  $ds$ , i.e. atmospheric emission, the variation of radiance is expressed by

$$dL_\nu = j_\nu n_a ds \Rightarrow dL_\nu = k_\nu n_a J_\nu ds. \quad (3.8)$$

Here,  $j_\nu$  is the emission coefficient. We define the source function as  $J_\nu = j_\nu/k_\nu$ . To complete the RTE we join the two parts, absorption and emission, along a optical path from  $s_0$  to  $s$  (Figure 3.2) at a fixed point (P),

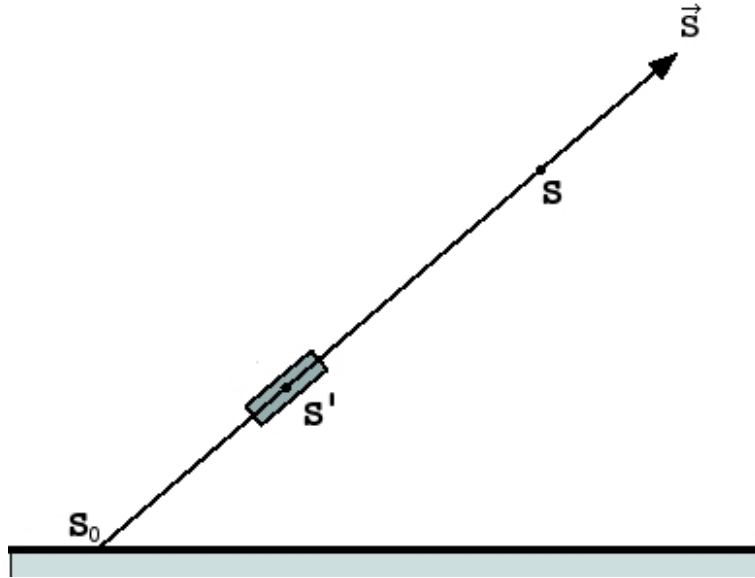


Figure 3.2: Graphical definition of optical path.

$$\frac{dL_\nu(P, \mathbf{s})}{ds} = -k_\nu n_a [L_\nu(P, \mathbf{s}) - J_\nu(P, \mathbf{s})]. \quad (3.9)$$

This is the basic form of the Radiative Transfer Equation. We can also express it in terms of the heating rate (Eq. 3.6) and the definition of the radiative flux as a

<sup>2</sup>The intensive quantity used to describe the degree of concentration of countable objects. In this case the number of atmospheric molecules per volume.



function of radiance (Eq. 3.2). Thus the Equation 3.9 integrated over all solid angles can be written as follows:

$$h_\nu(P) = 4\pi k_\nu n_a \left( \bar{L}_\nu(P) - \bar{J}_\nu(P) \right), \quad (3.10)$$

where  $\bar{L}_\nu(P)$  and  $\bar{J}_\nu(P)$  are the incident radiance and the source function averaged over all solid angles:

$$\bar{L}_\nu(P) = \frac{1}{4\pi} \int_{\omega} L_\nu(P, \mathbf{s}) d\omega, \quad (3.11)$$

$$\bar{J}_\nu(P) = \frac{1}{4\pi} \int_{\omega} J_\nu(P, \mathbf{s}) d\omega. \quad (3.12)$$

At this point we introduce a parameter which controls the absorption of light between two points,  $s$  and  $s'$ , along the optical path, the optical thickness,  $\tau_\nu(s, s')$ :

$$\tau_\nu(s, s') = \int_{s'}^s k_\nu(s'') n_a(s'') ds''. \quad (3.13)$$

It is important to remark some points: *a)* we take  $s > s'$  so; *b)*  $\tau_\nu(s, s')$  is a positive quantity and, as a consequence; *c)* the quantity  $d\tau_\nu/ds$  is negative. Introducing this definition in the RTE we obtain:

$$\frac{dL_\nu}{d\tau_\nu} = L_\nu(s', s) - J_\nu(s', s). \quad (3.14)$$

Now the RTE is described as a first order ordinary differential equation with the formal solution:

$$L_\nu(s, \mathbf{s}) = L_\nu(s_0, \mathbf{s}) e^{-\tau(s_0, s)} + \int_{s_0}^s k_\nu(s') n_a(s') J_\nu(s', s) e^{-\tau(s', s)} ds'. \quad (3.15)$$

This equation describes the radiance at  $s$  in the direction  $\mathbf{s}$ ,  $L_\nu(s, \mathbf{s})$ , after passing through the optical path from  $s_0$  to  $s$  in a given medium. In this case  $k_\nu(s)$  and  $n_a(s)$  are the absorption coefficient and the absorbing molecules' density along the optical path, respectively. The first term of the equation,  $L_\nu(s_0, \mathbf{s}) e^{-\tau(s_0, s)}$ , expresses the initial radiance at  $s_0$  (radiance from the Sun, the deep space or the Earth's surface) and its attenuation, the exponential part, between  $s_0$  and the observation point  $s$ . The second term expresses the contributions (emissions) of all the volume elements at positions  $s'$  along the path reduced in their corresponding absorptions.

### 3.2.1. Radiative Transfer Equation for Limb Observations

MIPAS measures the radiance emitted by the atmosphere using the limb sensing technique (Figure 3.3). Hence we need to adapt the Radiative Transfer Equation (RTE) to limb observations. The limb radiance, with tangent point  $x_t$ , observed from direction  $\vec{x}$  is obtained by convolution of the radiance emitted by the atmosphere at

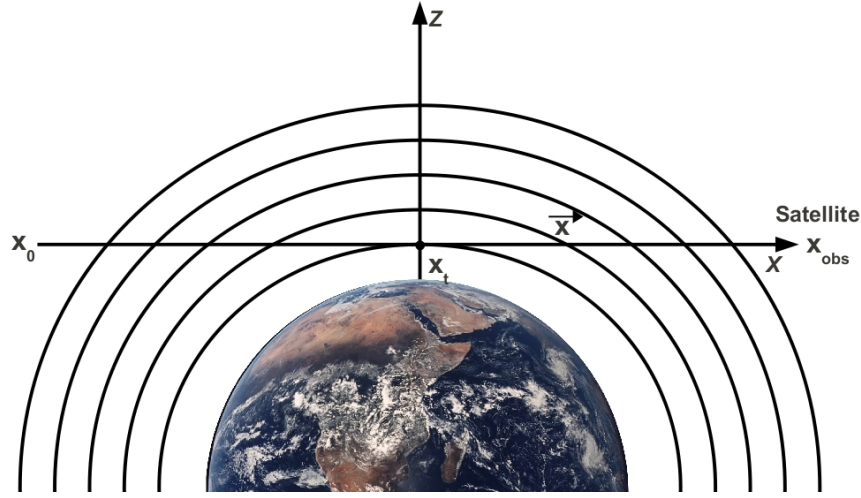


Figure 3.3: Earth limb observation geometry.

frequency  $\nu$  with the instrumental response function  $F(\nu)$  and over a finite range of frequency,  $\Delta\nu$ ,

$$L_{instr}(x_{obs}, \mathbf{x}) = \int_{FOV} \int_{\Delta\nu} L_{\nu}(x_{obs}, \mathbf{x}) F(\nu) d\nu d\omega, \quad (3.16)$$

where  $L_{\nu}(x_{obs}, \mathbf{x})$  is the monochromatic limb radiance at a given observation point  $x_{obs}$  and in the direction of the line of sight vector  $\mathbf{x}$ . At this point we introduce the transmittance, the exponential part of the RTE:

$$T_{\nu}(x, x_{obs}) = \exp[-\tau_{\nu}(x, x_{obs})] = \exp\left(-\int_x^{x_{obs}} k_{\nu}(x') n_a(x') dx'\right). \quad (3.17)$$

Considering this definition and assuming that the background radiation,  $L_{\nu}(x_0)$  is zero, we can rewrite Eq. 3.15 as follows

$$L_{\nu}(x_{obs}, \mathbf{x}) = \int_{x_0}^{x_{obs}} J_{\nu}(x) \frac{dT_{\nu}(x, x_{obs})}{dx} dx. \quad (3.18)$$

### 3.2.2. Discretization of the RTE

In this work we need to simulate the limb radiance in order to compare with the real measurements. This modeling using a numerical code is known as the forward problem. In our case we use a numerical solution of the RTE which divides the atmosphere in homogeneous layers. For that reason, it is useful to divide the whole atmosphere in concentric layers of constant temperature, pressure and density. We define the density of the absorbing gas,  $n_l$ , the absorption coefficient,  $k_{\nu,l}$ , and the source function,  $J_{\nu,l}$ , as constants within each atmospheric layer  $l$ , between,  $x_l$  and  $x_s$ . First, it is necessary to define the optical mass or absorbing amount,  $u_l$  in the

direction of  $\mathbf{x}$ , as the density between  $n_s$  and  $n_l$  times the distance, i.e.,

$$u_l(\mathbf{x})_l(x_s - x_l). \quad (3.19)$$

The optical thickness of the layer  $l$  in the direction of  $\mathbf{x}$  can be expressed as:

$$\tau_{\nu,l}(\mathbf{x}) = \tau_{\nu,l}(x_s, x_s) = k_{\nu,l}u_l(\mathbf{x}). \quad (3.20)$$

Thus, once we have all the information to describe the RTE (Eq. 3.18) in a discrete form, we change the integration by a sum over all the layers involved as follows:

$$L_{\nu}(x_{obs}, \mathbf{x}) = \sum_{l=0}^N \left[ J_{\nu,l} (1 - \exp[-k_{\nu,l}u_l(\mathbf{x})]) \prod_{j>l} \exp(-k_{\nu,j}u_j(\mathbf{x})) \right], \quad (3.21)$$

where the layer  $l = 0$  is located at  $x_0$ . The next step is to determine the source function,  $J_{\nu}$ , that depends on the interaction between the radiative field and matter.

### 3.3. Non-Local Thermodynamic Equilibrium (non-LTE)

#### 3.3.1. Local Thermodynamic Equilibrium (LTE) and Breakdown Conditions

Schwarzschild introduced the concept of LTE in 1906 when studying stellar atmospheres. He was wondering about the possibility to assume equilibrium not in the whole atmosphere but in gas parcels as a close approximation to reality. These gas parcels are composed of atoms and molecules with excited electronic, vibrational and rotational energy levels which interact with a radiative field.

If we consider a gas parcel completely enclosed and isolated from the rest of the atmosphere, it will eventually becomes in thermodynamic equilibrium. This condition allow us to define a common macroscopic quantity within this region, the temperature of the gas parcel.

Under these conditions, the energy emitted by the components of this gas parcel in thermodynamic equilibrium at a certain frequency,  $\nu$ , can be described by the Planck function. According to Planck's law, the electromagnetic radiation emitted by a black body in thermal equilibrium is given by

$$B_{\nu}(T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1}, \quad (3.22)$$

where  $h$  is the Planck's constant,  $k$  is the Boltzmann's constant and  $c$  is the speed of light. The absorption at a given frequency also depends only on the particular gas and temperature.

The molecular and atomic velocities distribution is given by the Maxwellian distribution at that temperature:

$$n du = 4\pi N \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} u^2 \exp\left( -\frac{mu^2}{2kT} \right) du, \quad (3.23)$$

where  $n dv$  is the number of particles with a velocity between  $u$  and  $u + du$ ,  $N$  is the total number of particles and  $m$  is the mass of a single one. The kinetic energy is expressed as function of temperature:

$$E_k = \frac{3}{2} kT. \quad (3.24)$$

In a real atmosphere, thermodynamic equilibrium is not fulfilled. In this way, an accurate approximation is to take the neighboring parcel of gas described as if it were in thermodynamic equilibrium and ruled by a 'local' kinetic temperature  $T_k$ . This is the Local Thermodynamic Equilibrium (LTE) case. In this situation, the source function  $J_\nu(T)$  can be approximated by  $B_\nu(T_k)$ . It is important to note, however that the radiance of the radiative field,  $L_\nu$ , is not necessarily be given by the Planck function  $B_\nu(T_k)$ . The velocities distribution and the kinetic energy are given by the same expression above but at the local kinetic temperature  $T_k$ .

Then, in LTE, the redistribution of the kinetic energy of molecules occurs very quickly, much more quickly than the redistribution with other energy forms such as radiation or internal energy. The population distribution of the excited levels is given by the Boltzmann's law:

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left( -\frac{E_i - E_j}{kT_k} \right), \quad (3.25)$$

where  $i$  and  $j$  indicates the two states involved in the transition;  $n_i$  and  $n_j$  their respective population;  $g_i$  and  $g_j$  their degeneracies and  $E_i$  and  $E_j$  their energies. Therefore we can describe the emission at a given wavelength and the populations of the excited levels involved by using the local kinetic temperature,  $T_k$ .

In a planetary atmosphere, where kinetic energy transfer prevails, the approximation of LTE provides an accurate representation of the realistic case. Of course we will find temperature gradients but they are caused by the different vicinities where thermodynamic equilibrium dominates, i.e., each gas parcel neighborhood defines different kinetic temperatures depending on altitude,  $T_k(z)$ .

The LTE treatment is, however, unable to describe the radiative properties of a gas parcel under many other physical conditions. For example, when thermal collisions are not fast enough to provide the energy lost by radiation (spontaneous emission), or when the energy levels are over-populated by an external (e.g. the solar) radiative field. An appropriate treatment of them requires the inclusion of non-LTE. The concept of non-LTE was introduced in the context of stellar atmospheres by Milne in 1930 (Milne, 1930). After this first treatment, this subject has been extensively studied in astrophysics, mainly to interpret stellar spectra and to study line formation

in hot stars. A detailed description of non-LTE applied to planetary atmospheres, and the Earth's atmosphere in particular, is given by (López-Puertas and Taylor, 2001) and a brief summary and a few examples in (López-Puertas and Funke, 2015).

In addition to the two general examples given above, LTE is not applicable when the following processes become important:

- *Collisional vibrational-vibrational processes (V-V)*: Involving energy exchange between two or more vibrational states. For example, the exchange of CO<sub>2</sub>  $\nu_3$  quanta and N<sub>2</sub>(1), very important for the understanding of CO<sub>2</sub> radiation at 4.3  $\mu\text{m}$ .
- *Electronic-vibrational processes (E-V)*: Involving electronic relaxation for one molecule and vibrational excitation of the partner. Like the excitation of N<sub>2</sub> by the electronically excited O(<sup>1</sup>D).
- *Chemical recombination*: The energy of a vibrational excited molecule comes from the chemical energy of a reaction. For example, the O<sub>3</sub> excitation from the recombination process  $O_2 + O + M \rightarrow O_3(v) + M$ , or the excitation of the hydroxyl radical (OH) from the Bates-Nicolet reaction,  $O_3 + H \rightarrow O_2 + OH(v \leq 9)$ .
- *Photochemical reactions*: From reactions induced by the solar radiance like the photolysis of the ozone in the Hartley band.
- *Dissociative recombination*: The most common is  $O_2^+ + e^- \rightarrow O^* + O$ .
- *Collisions with charged particles*: For example during auroras and proton events.

All these situations lead to non Local Thermodynamic Equilibrium (non-LTE) populations. The most common scenarios for non-LTE emissions occur at high altitudes, where pressure is low and collisions infrequent. As we mention before, pressure is not high enough to make thermal processes to compensate for the energy gained by other processes described above or lost by the radiative processes as spontaneous emission. For the vibrational transitions we can find non-LTE emissions above 60 km (CO<sub>2</sub> at 4.3  $\mu\text{m}$ ), 90 km (CO<sub>2</sub> at 15  $\mu\text{m}$ ) and others such as O<sub>3</sub> hot bands at 30-40 km or NO 5.3  $\mu\text{m}$  fundamental band from 20 km.

To understand the radiative emission in non-LTE it is essential to know all the microscopic processes populating the different energy levels involved (Figure 3.4). The Statistical Equilibrium Equation (SEE), further explained below, expresses the balance between all these processes and provides the level populations.

The thermal collisions, ruled by the kinetic temperature and density (pressure), loose importance as the non-LTE conditions go on stage. Thus the energy transfer involving radiative transitions and vibrational-vibrational processes prevails. We can then introduce the quantity of vibrational or rotational temperature to describe the

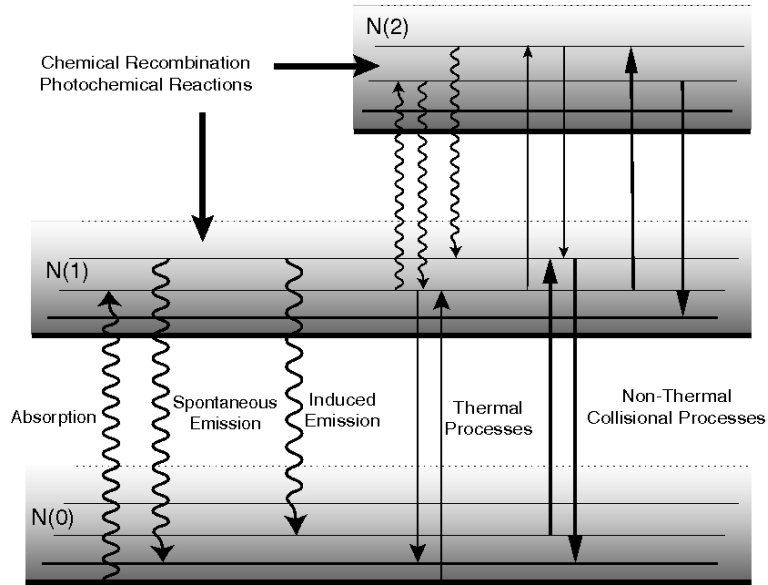


Figure 3.4: Microscopic processes affecting the populations of the vibrational states of molecule N.

population of the vibrational/rotational energy levels, e.g.,

$$\frac{n_{v,r}}{n_0} = \frac{g_{v,r}}{g_0} \exp\left(-\frac{E_{v,r}}{kT_{v,r}}\right), \quad (3.26)$$

where lower-case expression  $v,r$  indicates a given vibrational or rotational state. Then  $n_{v,r}$  is the number density of the upper state,  $E_{v,r}$  its energy,  $g_{v,r}$  its degeneracy,  $T_{v,r}$  its vibrational/rotational temperature,  $n_0$  is the number density of the lower state and  $g_0$  its degeneracy. If the vibrational/rotational temperature differs from the kinetic temperature we have then non-LTE conditions.

### 3.3.2. The Source Function for Non-LTE

As we described above, in a gas parcel in non-LTE, the source function cannot be described by the Planck function. Hence, this function,  $B_\nu(T)$ , is not representative of the emissions from the different atoms and molecules. In order to characterize the emission we must find a form for the source function. For this purpose we need to solve the radiative transfer and statistical equilibrium equations, RTE and SEE, simultaneously.

Regarding SEE, firstly we consider a sample of gas interacting with the radiative field,  $L_\nu$ . The spontaneous emissions and induced absorption and emission were described by Einstein by introducing the A and B coefficients. These coefficients depend only on the intrinsic quantum properties of the molecules and transitions so they are independent of the thermodynamic state of the gas and of the radiative field. Considering a lower level (1) and an upper level (2), the Einstein coefficients

are related by

$$\frac{A_{21}}{B_{21}} = \frac{2h\nu_0^3}{c^2} \quad \text{and} \quad \frac{B_{12}}{B_{21}} = \frac{g_2}{g_1}, \quad (3.27)$$

where  $\nu_0$  is the frequency of the vibrational transition or band centre,  $A_{21}$  is related to the spontaneous emission,  $B_{21}$  with the induced emission and  $B_{12}$  with absorption.

For the next step is necessary to establish the balance of absorbed and emitted photons when radiation interacts with matter. The change in the radiance along a path  $ds$  and over a solid angle  $d\omega$  can be expressed as:

$$\frac{1}{h\nu} \frac{dL_\nu}{ds} d\omega = (n_2 A_{21} + n_2 B_{21} L_\nu - n_1 B_{12} L_\nu) \frac{d\omega}{4\pi}. \quad (3.28)$$

The source function and the absorption coefficient can be expressed using the equation for the Einstein coefficients (Eq. 3.27) and the RTE (Eq. 3.9):

$$k_\nu = \frac{h\nu}{4\pi} \frac{n_1}{n_a} B_{12} \left(1 - \frac{g_1 n_2}{g_2 n_1}\right), \quad (3.29)$$

$$J_\nu = \frac{2h\nu^3}{c^2} \left(\frac{g_2 n_1}{g_1 n_2} - 1\right)^{-1}. \quad (3.30)$$

It is necessary to take into account the case when the width of the band is not negligible ( $\nu - \nu_0 \neq 0$ ). With this assumption the absorption coefficient is considered over an interval of frequency  $\Delta\nu$ .

Regarding the population ratio,  $n_2/n_1$ , appearing in the equations above, if we consider non-LTE emissions, we need to take into account all populating and depopulating processes affecting the different vibrational levels involved. There are radiative processes, thermal collisions and non-thermal collisions (see Fig. 3.4):

- *Radiative processes*: they include the spontaneous and induced emission and absorption. The number of molecules radiatively absorbed per unit of volume is  $B_{12} n_1 \bar{L}_\nu^3$ . The number of emitted molecules is  $A_{21} n_2 + B_{21} n_2 \bar{L}_\nu$ .
- *Thermal collisions*: constituted by the before-mentioned vibrational-translational collisions (V-T):

$$k_t : n_2 + M \rightleftharpoons n_1 + M + \Delta E, \quad (3.31)$$

where  $M$  is any air molecule,  $k_t$  is the collisional thermal rate and  $\Delta E = E_2 - E_1 = h\nu_0$  is the energy difference of the upper and lower levels. The number of molecules de-excited from level 2 to level 1 by thermal collisions is  $l_t = k_t[M]$  and the excited ones is  $p_t = k'_t[M]$ . Where  $k'_t$  is the inverse

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<sup>3</sup> $\bar{L}_\nu$  is the radiance averaged over all solid angles.

collisional rate related to  $k_t$  by a detailed balance:

$$k'_t = k_t \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{kT}\right). \quad (3.32)$$

■ *Non-thermal collisional processes:*

$$k_{vv} : \quad n_1 + C(\nu) \rightleftharpoons n_2 + C(\nu') + \Delta E_\nu, \quad (3.33)$$

$$k_{ev} : \quad N^* + n_1 \rightarrow n_2 + N + \Delta E_{ev}, \quad (3.34)$$

$$k_c : \quad A + B + M \rightarrow n_2 + M, \quad (3.35)$$

at rates  $k_{vv}$ ,  $k_{ev}$  and  $k_c$ .  $C(\nu)$  is an atmospheric molecule excited in vibrational level  $\nu$  before, and  $\nu'$  after, the collision; and  $N^*$  is an excited atom or a molecule electronically or vibrationally excited.  $\Delta E_\nu = E_\nu - E_{\nu'} - h\nu_0$  and  $E_{ev} = E^* - h\nu_0$  are the energy excesses, with  $E^*$  being the energy of  $N^*$ .  $p_{nt} = k_{vv}[C(\nu)] + k_{ev}[N^*] + k_c[A][B]/n_1$  is the specific production rate of  $n_2$  molecules due to the non-thermal processes (Eqs. 3.33, 3.34 and 3.35), and the specific loss rate of  $n_2$  in non-thermal processes (Eq. 3.33) is  $l_{nt} = k'_{vv}[C(\nu')]$ .

In order to balance the excitation and de-excitation processes we set the conservative principle of steady state and define the Statistical Equilibrium Equation (SEE):

$$n_1(B_{12}\bar{L}_\nu + p_t + p_{nt}) = n_2(B_{21}\bar{L}_\nu + A_{21} + l_t + l_{nt}), \quad (3.36)$$

where all the processes described above are included. The lefthand side of the equation express the productions and the righthand side the losses of level  $n_2$ . In this way we can describe the population ratio as follows:

$$\frac{n_2}{n_1} = \frac{B_{12}\bar{L}_\nu + p_t + p_{nt}}{A_{21} + B_{21}\bar{L}_\nu + l_t + l_{nt}}. \quad (3.37)$$

Using this form of the SEE, the Einstein relations (3.27) and the source function (3.30) we can write the source function centered at  $\nu_0$  for the two levels approach as follows:

$$J_{\nu_0} = \frac{\bar{L}_{\Delta\nu} + \epsilon_1 B_{\nu_0}}{1 + \epsilon_2}, \quad (3.38)$$

where  $\epsilon_1$  and  $\epsilon_2$  are

$$\epsilon_1 = \frac{p_t + p_{nt}}{A_{21}} \frac{g_1}{g_2} \left[ \exp\left(\frac{h\nu}{kT_k}\right) - 1 \right]; \quad \text{and} \quad \epsilon_2 = \frac{l_t + l_{nt}}{A_{21}} \left( 1 - \frac{p_t + p_{nt}}{l_t + l_{nt}} \frac{g_1}{g_2} \right). \quad (3.39)$$

This form of the source function is called the integral equation and depends on the unknown mean radiance over a spectral band,  $\bar{L}_{\Delta\nu}$ , and other known parameters such as the Planck function, the Einstein coefficients, and the collisional rates.



### 3.4. Solving the Non-LTE Problem

At this point the RTE (3.15) and the SEE (3.36) are expressed in forms which are interdependent. Both equations form a system of coupled equations. Thus obtaining of an analytical solution is not possible and the system must be resolved using a numerical method. To resolve the general case we must consider: i) the energy transfer between atmospheric layers; ii) external radiation fields (such as solar or Earth's surface radiations); iii) the strong dependence of the absorption coefficient on frequency; iv) all the processes described before affecting the vibrational-rotational states of the molecules and; v) the V-V collisional coupling between some vibrational levels. There are different techniques to resolve the integrations over frequency, solid angle and altitude of the system RTE and SEE equations.

A commonly used approach is the Curtis matrix method (Curtis, 1956; López-Puertas and Taylor, 2001) which algebraically solves a combination of SEE and linearized RTE for two levels systems connected by particular radiative transitions, sequentially for all the considered levels. Since the SEE and RTE are solved simultaneously, this method is computationally less expensive. However, it includes approximations related to linearized radiative transfer, and requires iterations between the two-levels systems of energy levels that are strongly coupled by V-V collisions.

This method uses the RTE in the form of the heating rate for the two levels approach (levels 2 and 1), which, using the definition of the ro-vibrational band strength,  $S^4$ , takes the form:

$$h_{12} = 4\pi S n_a [\bar{L}_{\Delta\nu} - J_{\nu_0}]. \quad (3.41)$$

Introducing this equation into the equation for the source function, (3.38), we obtain the source function at each layer  $i$ :

$$J_{\nu_0,i} = \frac{\epsilon_{1,i}}{\epsilon_{2,i}} B_{\nu_0,i} + \frac{1}{4\pi S_i n_{a,i} \epsilon_{2,i}} h_{12,i}. \quad (3.42)$$

The Curtis matrix has an order of  $N \times N$ , where  $N$  is the number of atmospheric layers. Each matrix element,  $C_{ij}$ , represents the radiative transfer between all atmospheric layers and boundaries. The diagonal elements represent the cooling to space of the  $i^{th}$  layer and the non-diagonal elements of the radiative contribution represent the layer  $j^{th}$  to the  $i^{th}$  net heating rate. With  $C_{ij}$  we can re-write the heating rate as:

$$h_i = \sum_j C_{ij} J_{\nu_0,j} + h_{l,i} + h_{u,i}, \quad (3.43)$$

where the heating rates from the lower and upper boundaries layer are  $h_{l,i}$  and

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<sup>4</sup>The band strength is given by:

$$S = \int_{\Delta\nu} k_\nu d\nu. \quad (3.40)$$

$h_{u,i}$  respectively. At the lower boundary of the atmosphere, the Earth's surface emission is usually taken by a Planck function at surface's kinetic temperature. Since radiation coming from space is negligible, we take into account solely the incoming solar radiation for the upper boundary.

The last two equations, (3.42) and (3.43), form a linear system for all atmospheric layers. The heating rates and the source function are the unknown quantities. In matrix form, we can write:

$$\mathbf{h} = \mathcal{C}\mathbf{J} + \mathbf{h}_b \quad ; \quad \mathbf{J} = \mathcal{E}\mathbf{B} + \mathcal{D}\mathbf{h}, \quad (3.44)$$

where  $\mathbf{h}_b$  is the sum  $\mathbf{h}_l + \mathbf{h}_u$ ,  $\mathcal{C}$  is the Curtis matrix,  $\mathcal{D}$  and  $\mathcal{E}$  are both diagonal matrices given by:

$$\mathcal{E} = \frac{\epsilon_{1,i}}{\epsilon_{2,i}} \quad ; \quad \mathcal{D} = \frac{1}{4\pi S_i n_{a,i} \epsilon_{2,i}}. \quad (3.45)$$

If the radiative coupling between layers is important, the Curtis matrix method allows for an accurate solution without the need of iterations.

A different method for solving the combined SEE+RTE is by iterating between the statistical equilibrium and transfer equations. Commonly referred as Lambda iteration, it alternates SEE calculations involving all the energy levels with RTE calculations involving all atmospheric layers. The main disadvantage of Lambda iteration is the slow convergence in optically thick conditions. Therefore, different acceleration strategies, like the Accelerated Lambda Iteration (ALI) techniques (Kutepov et al., 1991; Rybicki and Hummer, 1991), have been employed in practical applications.

The advantages of both methods can be combined by optionally including Curtis matrix-type algebraical solutions of the RTE into the Lambda iteration in order to speed up the convergence.

### 3.5. The Inverse Problem

In order to derive atmospheric quantities from remotely sensed atmospheric radiances, we have to invert the forward problem, i.e., to solve the inverse problem. In this way we can retrieve pressure, temperature, density or gases abundances from measured atmospheric radiances. There are two main difficulties regarding the inverse problem: i) to go from discrete measurements to the retrieval of continuous profiles; and ii) the non-linearities of the retrieval equations. A theory of the inversion problem applied to atmospheric measurements is presented by Rodgers (2000).

Let us begin considering a certain vector of measurements,  $\vec{y}$ , typically a set of observed spectra, with  $m$  dimensions and a vector of retrieval parameters,  $\vec{x}$ , with  $n$  dimensions. The forward problem can be expressed as

$$\vec{y} = \mathbf{F}(\vec{x}), \quad (3.46)$$

where  $\mathbf{F}(\vec{x})$  is a non-linear function representing the radiative transfer equation depending on the retrieval parameter. When resolving the inverse problem we aim to calculate  $\vec{x} = \mathbf{f}(\vec{y})$ .

If we include random errors  $\vec{\epsilon}$  due to the instrumentation, the forward problem can be written as

$$\vec{y} = \mathbf{F}(\vec{x}) + \vec{\epsilon}. \quad (3.47)$$

The radiative transfer problem (3.47) can be linearised with respect to a reference state,  $\vec{x}_0$ , as

$$\vec{y} = \mathbf{F}(\vec{x}_0) + \mathbf{K}(\vec{x} - \vec{x}_0) + \vec{\epsilon}, \quad (3.48)$$

where  $\mathbf{K}$  is the Jacobian, a matrix of  $m \times n$  dimensions:

$$\mathbf{K} = \frac{\delta \mathbf{F}(\vec{x})}{\delta \vec{x}}. \quad (3.49)$$

Physically, the Jacobian expresses the sensitivity of the measurement with respect to a given parameter. The rank of  $\mathbf{K}$  is  $p$  and denotes the number of linearly independent rows which form a subspace within the state space. If this subspace is lower than the state space,  $p < n$ , there is a null space where the solution can take any value because it is not determined by the measurements. For instance, this can occur when the profile to be retrieved covers a vertical range not of sounded by the instrument. The characterization of the null space is essential for the resolution of the inverse problem. This space identifies how many measures are necessary to provide information of the retrieval parameter.

The measurement errors are represented by the covariance matrix,  $\mathbf{S}_y$ . The elements of the covariance matrix are given by

$$S_{ij} = \langle (\epsilon_i - \langle \epsilon_i \rangle)(\epsilon_j - \langle \epsilon_j \rangle) \rangle, \quad (3.50)$$

where  $\epsilon_{i,j}$  are the errors of the measurements  $i$  and  $j$ .

An usual form of resolving the inverse problem (3.47) is by minimizing the quadratic sum of the difference of the measure vector and the forward problem,  $[\vec{y} - \mathbf{F}(\vec{x})]^2$ , weighted with  $\mathbf{S}_y$ :

$$\frac{\delta}{\delta \vec{x}} ([\vec{y} - \mathbf{F}(\vec{x})]^T \mathbf{S}_y^{-1} [\vec{y} - \mathbf{F}(\vec{x})]) = 0 \quad (3.51)$$

that, because of its non-linearity, have to be solved iteratively, i.e.,

$$\vec{x}_{i+1} = \vec{x}_i + [\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K}]^{-1} \times [\mathbf{K}^T \mathbf{S}_y^{-1} (\vec{y} - \mathbf{F}(\vec{x}))]. \quad (3.52)$$

At this point we need *a priori* information to characterize the components of the state vector belonging to the null space,  $\vec{x}_a$ . The process of introducing additional information in order to resolve an ill-posed problem is called regularization. This is

done by including the regularization matrix  $\mathbf{R}$ . We can think about it as a function that fills the gaps of information and provides a character of continuity to the measurements. The retrieval equation is then written as

$$\vec{x}_{i+1} = \vec{x}_i + \left[ \mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R} \right]^{-1} \times \left[ \mathbf{K}^T \mathbf{S}_y^{-1} (\vec{y} - \mathbf{F}(\vec{x})) - \mathbf{R}(\vec{x}_i - \vec{x}_a) \right]. \quad (3.53)$$

The selection of a certain regularization depends on how accurate the *a priori* information is. Rodgers (2000) propose the "optimal estimation" or "maximum *a posteriori*" methods when a certain knowledge on the *a priori* information is given. In these cases the regularization matrix is equal to the covariance matrix of the *a priori* information,  $S_a$ . The information is generally obtained from climatological data known beforehand. This method provide the best trade-off between the retrieval random errors and the degrees of freedom, i.e. the number of independent pieces of information contained in the measurements.

Another option to define the regularization matrix is the Tikhonov formalism (Tikhonov, 1963). In this method the regularization matrix,  $\mathbf{R}$ , is given by  $\gamma \mathbf{B}^T \mathbf{B}$ , where  $\gamma$  represents the weight of the measurements versus the *a priori* information and  $\mathbf{B}$  the matrix that defines the order of the regularization. The main advantage of the Tikhonov regularization of orders greater than zero is the independence of the results on the absolute value of the *a priori*. Zero-order Tikhonov regularization, that is  $\mathbf{B} = \mathbf{I}$ , is equivalent to optimal estimation with a diagonal covariance matrix. It minimizes the mean differences  $\vec{x} - \vec{x}_a$ . This method is useful if the retrieval parameter is known to be close to the *a priori* values. The first-order Tikhonov regularization minimizes the derivative of the mean differences  $\vec{x} - \vec{x}_a$ , in this case:

$$\mathbf{B} = \begin{pmatrix} -1 & 1 & 0 & 0 & \dots \\ 0 & -1 & 1 & 0 & \dots \\ 0 & 0 & -1 & 1 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \quad (3.54)$$

This order is useful when the profile shape of the solution and of the *a priori* are expected to be close. Regarding the second-order regularization, it minimizes the second derivative of  $\vec{x} - \vec{x}_a$  avoiding, strong oscillations. The form of  $\mathbf{B}$  in this case is written as:

$$\mathbf{B} = \begin{pmatrix} -1 & 2 & 1 & \dots & \dots & \dots \\ 0 & -1 & 2 & 1 & \dots & \dots \\ 0 & 0 & -1 & 2 & 1 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \quad (3.55)$$

As we mentioned above, the inverse problem is non-linear so the linear approximation of  $\vec{x}$  described must be forced within a given  $\vec{x}$  iteration. The Levenberg-Marquardt damping is used to avoid problems with strong non-linearities (Levenberg, 1944; Marquardt, 1963). In this way we include a damping term,  $\lambda \mathbf{I}$ , into Eq. (3.53) to give:

$$\vec{x}_{i+1} = \vec{x}_i + \left[ \mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R} + \lambda \mathbf{I} \right]^{-1} \times \left[ \mathbf{K}^T \mathbf{S}_y^{-1} (\vec{y} - \mathbf{F}(\vec{x})) - \mathbf{R}(\vec{x}_i - \vec{x}_a) \right]. \quad (3.56)$$

Within a given iteration the  $\lambda$  parameter is chosen depending on the value of  $\chi^2$  (this is described below). There are two options: i) if the  $\chi^2$  decreases in the iteration, a new  $\vec{x}_i$  is calculated and  $\lambda$  is decreased before proceeding to the next iteration; and ii) if  $\chi^2$  increases,  $\vec{x}_i$  is kept constant,  $\lambda$  is increased and starts a new iteration. This process is repeated until  $\lambda$  decreases.

Rodgers (2000) defines the gain matrix,  $\mathbf{G}$ , to express how the measurements,  $\vec{y}$ , maps into the retrieved parameters,  $\vec{x}$ . Hence it is the transformation of the measure space into the parameters space.  $\mathbf{G}$  is given by:

$$\mathbf{G} = \left( \mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R} \right)^{-1} \mathbf{K}^T \mathbf{S}_y^{-1}. \quad (3.57)$$

The gain matrix performs the inverse transformation of the Jacobian. The averaging kernel matrix,  $\mathbf{A} = \mathbf{G}\mathbf{K}$ , describes how the true profile maps into the parameter space. In practice, particularly when the retrieval grid is finer than the measurement grid, the averaging kernel shows a broad diagonal structure with maximum values lower than 1. In an ideal case, if the retrieved values coincide with the true one,  $\mathbf{A}$  would be equal to the identity matrix. The full width at half maximum of either the columns or rows of  $\mathbf{A}$  provide the vertical resolution. The  $\mathbf{A}$  columns describes the sensitivity of the retrieval to a given perturbation of  $\vec{x}$ . In addition, the trace of the averaging kernel matrix gives the number of independent pieces of information, i.e. the degrees of freedom. Because of all these properties, the averaging kernel matrix,  $\mathbf{A}$ , is often used as a diagnostics tool to characterize the quality of the retrievals.

The  $\chi^2$  of the retrieval is calculated by

$$\chi^2 = [\vec{y} - \mathbf{F}(\vec{x})]^T \mathbf{S}_y^{-1} [\vec{y} - \mathbf{F}(\vec{x})] + (\vec{x} - \vec{x}_a)^T \mathbf{R} (\vec{x} - \vec{x}_a), \quad (3.58)$$

which give us a measure of the goodness of the retrieval. The smaller (close to unity) the better.

Regarding the error analysis, let us start using the gain matrix to express the random error covariance matrix. It provides the retrieval errors due to the instrumental noise:

$$\mathbf{S}_x = \mathbf{G} \mathbf{S}_y \mathbf{G}^T. \quad (3.59)$$

The retrieval error due to systematic error,  $\epsilon_s$ , in the parameter  $a_j$  are

$$\Delta \vec{x}_j = \mathbf{G} \cdot [\mathbf{F}(\vec{x}, a_j + \epsilon_s) - \mathbf{F}(\vec{x}, a_j)]. \quad (3.60)$$

For retrieving vertical profiles, Rodgers (2000) describe two main methods: i) global fitting, which consists of a simultaneous retrieval of the whole set of atmospheric layers; and ii) the onion peeling method, that consists in performing the retrieval from the higher layers to the lower ones sequentially.

In the next chapter we describe the radiative transfer code, Karlsruhe Optimized and Precise Radiative transfer Algorithm (KOPRA), the non-LTE code, Generic Radiative traNsfer AnD non-LTE population Algorithm (GRANADA) and the retrieval

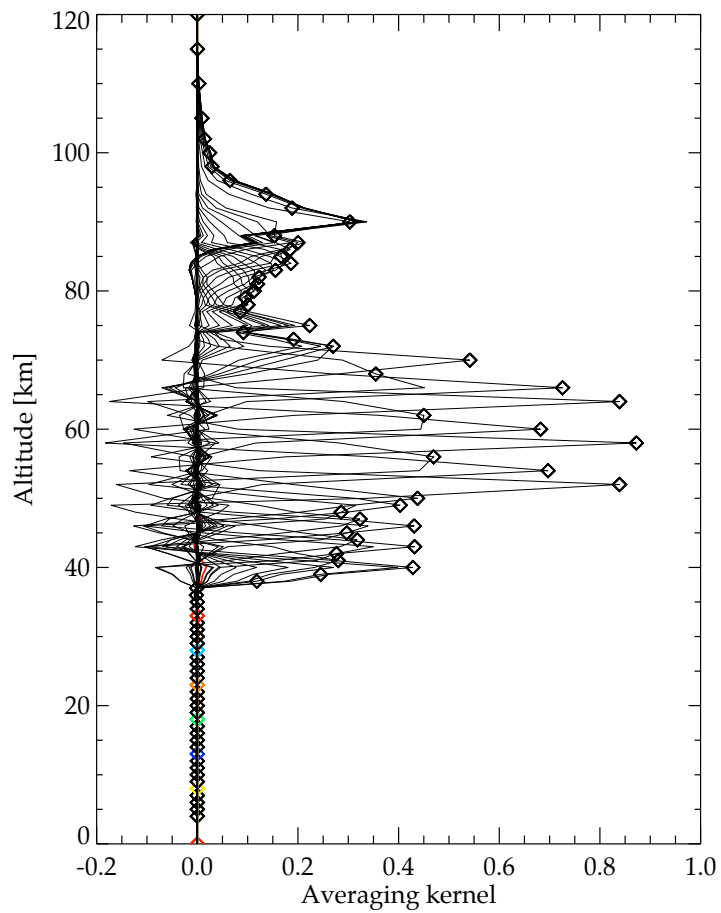


Figure 3.5: Normalized averaging kernel graphical representation of rows for the example of an  $O_3$  retrieval from MIPAS spectra taken in the NLC observation mode. Each line represents the information profile from each tangent altitude.

code, Retrieval Control Program (RCP) used in this work. These codes are used for solving the RTE for limb observations, the calculation of the non-LTE populations used in the RTE, and the retrieval of non-LTE parameters (collisional rate coefficients) and of  $CO_2$  abundance profiles.

## Chapter 4

# Models and Algorithms

### *Abstract*

In this chapter we describe the three major models/computer codes used in the IAA-IMK retrieval scheme, that is: i) the Karlsruhe Optimized and Precise Radiative transfer Algorithm (KOPRA), used for modelling the atmospheric radiative transfer; ii) the Generic RAdiative traNsfEr AnD non-LTE population Algorithm (GRANADA) that calculates the non-LTE populations of the different energy levels; and iii) the Retrieval Control Program (RCP), a constrained least squares algorithm for retrieving atmospheric profile parameters. In addition, within the GRANADA section, a more detailed description of the CO<sub>2</sub> non-LTE model is presented, where the main collisional and radiative processes that control the non-LTE populations of the CO<sub>2</sub> energy levels are discussed. Finally, we describe the setup of the IAA-IMK retrieval scheme.

### 4.1. KOPRA

The Karlsruhe Optimized and Precise Radiative transfer Algorithm, KOPRA, models the mid-infrared radiative transfer through the atmosphere. This code was devised at the Institut für Meteorologie und Klimaforschung, IMK (Karlsruhe, Germany) as a tool to simulate the atmospheric infrared ro-vibrational emission measured by the MIPAS instrument (Stiller et al., 2002, <http://www.imk-asf.kit.edu/english/312.php>). For this purpose, KOPRA uses the integrated radiative transfer Eq. 3.15 assuming the Curtis-Godson approximation. KOPRA calculates the infrared monochromatic radiance,  $L_\nu(x_{obs})$ , by using the line-by-line technique. It also provides Jacobians calculated in a quasi-analytical mode. Regarding the atmosphere, the radiative transfer modelling is based on a layer-by-layer approach, i.e., the partial gas columns and the Curtis-Godson means<sup>1</sup> are calculated for each path segment of the line of sight.

KOPRA takes into account the oblateness of the Earth for the calculation of the line of sight, and includes the refraction in a non-spherical atmosphere with horizontally inhomogeneous densities. Thus, the calculation of the ray tracing along the line of

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<sup>1</sup>The Curtis-Godson means are calculated for temperature, pressure and non-LTE/LTE population ratios.

sight is performed by using changes in the refractive index and in the terrestrial geometry. If cirrus clouds in the upper troposphere or polar stratospheric clouds cross the line of sight, KOPRA models the continuum extinction in the mid-infrared spectrum caused by particles. As mentioned before, KOPRA is specifically suited for the analysis of the MIPAS data but it is able to handle many other observational geometries from satellite or balloon observations, taking into account the field-of-view and the spectral response (AILS) of the given instrument.

In the middle and upper atmosphere, KOPRA is able to handle the non-LTE effects in the radiance signal of the atmosphere. The information on the non-LTE populations of the molecular states is provided by the code GRANADA (see next section).

The spectral lines are modeled using a Voigt profile, i.e., convolving the Lorentz and Doppler line shapes. Spectroscopic information is usually taken from the HITRAN database (Rothman et al., 2013) although it can also handle other spectroscopic databases.

An additive low-frequency contribution to the absorption coefficient takes into account effects such as the contribution of heavy molecules; the absorption bands induced by collisions of the pairs  $N_2-N_2$  and  $O_2-O_2$ , and overlapping of line wings from absorption bands like  $CO_2$  4.3  $\mu m$  or  $H_2O$  6.3  $\mu m$ . Also, other features can be handled like the line-mixing effect in the  $CO_2$  bands, and the horizontal inhomogeneities in temperature or gas abundances. The vibrational bands and isotopes of the gases to be included, the atmosphere parameter profiles, the spectral resolution or the altitude grid can be specified by the user. In this way, KOPRA can be used also as a tool to perform sensitivity tests of simulated radiances in dependence of reference atmosphere by using its numerous possibilities.

The validation of KOPRA with respect to GENLN2, Reference Forward Model (RFM) and Simulation Program for Infrared Radiative Transfer (SPIRT) was performed by von Clarmann et al. (2002). For all these reasons it can be concluded that KOPRA fulfills the requirements and accuracy to be included in any automated retrieval system. The implementation of the non-LTE in KOPRA was performed by the Instituto de Astrofísica de Andalucía, IAA.

## 4.2. GRANADA

The Generic RAdiative traNsfer AnD non-LTE population Algorithm, GRANADA, calculates the non-LTE state populations of molecular rotational, vibrational spin and electronic levels (Funke et al., 2012). GRANADA, written in Fortran 95, expresses the non-LTE populations as population ratios with respect to those in LTE,  $n_{\nu_j}^{non-LTE}/n_{\nu_j}^{LTE}$ , or as vibrational/rotational temperatures (see Eq. 3.26). Furthermore, GRANADA is also able to compute the heating/cooling rates of the involved vibrational bands. This information is used by KOPRA to calculate the infrared radiance from non-LTE emissions. GRANADA uses many inputs including, among others, the gas abundances, the temperature profiles, the considered states and transitions and the non-LTE processes (radiative and collisional) to be included.



The model solves the locally defined statistical equilibrium equations (SEE) (Eq. 3.36) for all the energy levels considered and the radiative transfer equations (RTE) (Eq. 3.15) for all the bands connecting these levels in a discrete atmosphere prescribed at given altitude levels. The processes taken into account into the SEE are the radiative, collisional and chemical productions and losses.

As we described in the previous chapter, the RTE+SEE system cannot be solved analytically and hence a numerical method must be employed. In this way, GRANADA uses the Curtis matrix and the Lambda iteration methods (or a combination of both) to reach a solution iteratively. More details on the specific way we use it for calculating the CO<sub>2</sub> populations in this work are given below in Sec. 4.3.

The statistical equilibrium calculations are carried out by solving, at a given altitude, the linear equation system resulting for the state vectors  $\mathbf{n}$  (population density) of all the energy levels considered by the inversion of the matrix equation  $\mathbf{W}\mathbf{n} = \mathbf{p}$ .  $\mathbf{W}$  is a matrix with  $n \times n$  dimensions which diagonal elements represent the radiative, collisional and chemical losses of state  $i$ , meanwhile the off-diagonal elements corresponds to the radiative and collisional productions from state  $j$ . The  $\mathbf{p}$  vector represents the chemical productions of state  $i$ .

Three options are available for the radiative transfer calculations: (i) the standard line-by-line radiative transfer in Lambda iteration; (ii) the modified Curtis matrix method with line-by-line radiative transfer; and (iii) the modified Curtis matrix method with the equivalent line approach (see more detailed description in Funke et al. (2012)). The latter allows for a significant acceleration of radiative transfer calculations by histogramming of ro-vibrational lines in bins of the logarithm of the line strength.

GRANADA also provides non-LTE corrections of the Jacobians calculated by KOPRA by taking into account the dependency of the non-LTE populations,  $n$ , on the retrieved parameter  $\vec{x}$  (e.g., temperature, gas concentrations or collisional rates). The correction of the KOPRA Jacobians is done as follows:

$$\mathbf{K} = \left. \frac{\partial \mathbf{F}(\vec{x})}{\partial \vec{x}} \right|_{n=cte} + \frac{\partial \mathbf{F}(\vec{x})}{\partial n} \times \frac{\partial n}{\partial \vec{x}}, \quad (4.1)$$

where  $\mathbf{F}(\vec{x})$  is the modelled radiance. The terms  $\left. \frac{\partial \mathbf{F}(\vec{x})}{\partial \vec{x}} \right|_{n=cte}$  and  $\frac{\partial \mathbf{F}(\vec{x})}{\partial n}$ , provided by KOPRA, express the sensitivity of the modelled radiance to the retrieved parameter and to the non-LTE populations, respectively. The derivatives  $\partial n / \partial \vec{x}$  are provided by GRANADA. Therefore, GRANADA can also be used to perform sensitivity tests of the vibrational temperatures to, for instance, changes in the rates of the collisional processes or in the reference atmosphere (temperature and gas concentrations).

### 4.3. The CO<sub>2</sub> non-LTE model

The setup of GRANADA applied to CO<sub>2</sub> populations presented by Funke et al. (2012) takes into account 134 vibrational levels. At this point we should make a

note on notation. There are usually two ways for expressing the vibrationally excited states of CO<sub>2</sub>, the old Herzberg notation  $(v_1, v_2^l, v_3)$ , more physically intuitive, and the most modern HITRAN notation  $(v_1, v_2, l, v_3, r)$ , adopted in the HITRAN database and easier to use in computer codes. In those notations  $v_j$  is the quantum number associated with the normal mode of vibration  $j$ ,  $l$  is the vibrational angular momentum quantum number associated with the degenerate bending mode 2, and  $r$  is the ranking index, which is unity for the highest vibrational level of a Fermi resonating group (Rothman and Young, 1981; Rothman et al., 2005). In this work we use both notations indistinctly. Table A.1 might be useful in this respect, since it shows the correspondence between the two notations for most of the levels studied here. Additionally, to simplify the notation for the collisional processes (some of which are common to several levels), we also use a "compressed" notation,  $(v_d, v_3)$ , where  $v_d = 2v_1 + v_2$ , independently of the values of  $l$  and  $r$ .

Thus, the GRANADA model version used here includes the <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O (isotopologue 1) levels up to (7,0), (6,1), (3,2) and (1,3); <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O (isotopologue 2) levels up to (4,0) and (4,1); <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O and <sup>16</sup>O<sup>12</sup>C<sup>17</sup>O (isotopologues 3 and 4) levels up to (3,0) and (1,1); and <sup>16</sup>O<sup>13</sup>C<sup>18</sup>O and <sup>16</sup>O<sup>13</sup>C<sup>17</sup>O (isotopologues 5 and 6) levels up to (1,0) and (1,1).

Due to the strong collisional coupling of CO<sub>2</sub> with N<sub>2</sub>( $v = 1$ ) via V-V energy transfer, vibrational populations of N<sub>2</sub>( $v \leq 1$ ) are also included in the non-LTE model calculations. The SEE for N<sub>2</sub>(1) is coupled into the SEE for the main CO<sub>2</sub> isotope (626). The CO<sub>2</sub> levels are connected by 695 radiative transitions, 39 of them considering full radiative transfer in the atmosphere. These transitions involve vibrational states up to (4,1) for the main isotopologue, (3,0) and (2,1) for the isotopologue 636, and (1,1) for the isotopologues 628 and 627. Below 20 km, the upwelling component from the troposphere is approximated by a Planck function with a temperature from an estimated emission altitude located between 7 and 20 km. Above 20 km, radiative transfer is calculated in this case using the Curtis matrix formalism. The SEE for N<sub>2</sub>(1) is coupled into the 00011 → 00001 band RTE calculation. The spectroscopic data for CO<sub>2</sub> bands used by Funke et al. (2012) has been updated here with the most recent HITRAN database of 2012 Rothman et al. (2013).

The collisional scheme of the CO<sub>2</sub> levels is described in detail in Funke et al. (2012), which is adapted here in Table 4.1. This GRANADA setup for CO<sub>2</sub> has been significantly updated, benefiting from several analysis of SABER and MIPAS. Thus, López-Puertas et al. (2004) studied the SABER CO<sub>2</sub> 4.3 μm nighttime radiance and found a larger excitation of N<sub>2</sub> by OH( $\nu$ ) than assumed in previous works; and López-Puertas et al. (2005) analysed MIPAS data of the CO<sub>2</sub> 4.3 μm emissions, as well as from other studies described below. Here we include a brief discussion of the major collisional processes. We should mention that this Table is not updated with the new collisional rates retrieved in this work, which are described in the next chapter (see Table 5.1).

The collisional deactivation of CO<sub>2</sub> by O,

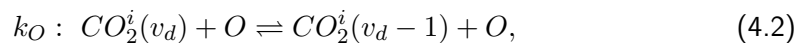


Table 4.1: Collisional rates that influences the CO<sub>2</sub> and N<sub>2</sub> vibrational levels (adapted from Funke et al., 2012).

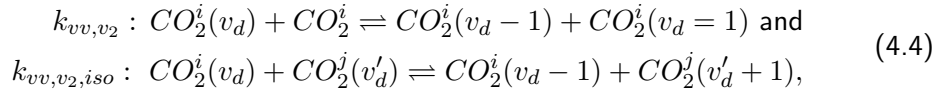
No.	Rate	Process	Rate coefficient <sup>†</sup>
1a	$k_{vt,v_2,N_2}$	$\text{CO}_2^i(v_d) + \text{N}_2 \rightleftharpoons \text{CO}_2^i(v_d - 1) + \text{N}_2$	$k \times 7 \times 10^{-17} \sqrt{T} + 6.7 \times 10^{-10} \exp(-83.8/T^{1/3})^\ddagger$
1b	$k_{vt,v_2,O_2}$	$\text{CO}_2^i(v_d) + \text{O}_2 \rightleftharpoons \text{CO}_2^i(v_d - 1) + \text{O}_2$	$k \times 7 \times 10^{-17} \sqrt{T} + 1.0 \times 10^{-9} \exp(-83.8/T^{1/3})^\ddagger$ ( $k=1, 3, 4.5, 6.75, 9, 12$ for $v_d = 1, \dots, 6$ )
1c	$k_O$	$\text{CO}_2^i(v_d) + \text{O} \rightleftharpoons \text{CO}_2^i(v_d - 1) + \text{O}$	$3.5 \times 10^{-13} \sqrt{T} + 2.32 \times 10^{-9} \exp(-76.75/T^{1/3})$
2a	$k_{vt,a}$	$\text{CO}_2^i(v_d, v_3) + \text{N}_2 \rightleftharpoons \text{CO}_2^i(v_d', v_3 - 1) + \text{N}_2, \Delta v_d=2-4$	$1.10 \times 10^{-15} + 1.14 \times 10^{-10} \exp(-72.3/\sqrt[3]{T}) + 2.3 \times 10^{-40} T^9$
2b	$k_{vt,b}$	$\text{CO}_2^i(v_d, v_3) + \text{O}_2 \rightleftharpoons \text{CO}_2^i(v_d', v_3 - 1) + \text{O}_2, \Delta v_d=2-4$	$1.82 \times 10^{-15} + 3.10 \times 10^{-11} \exp(-63.3/\sqrt[3]{T}) + 2.0 \times 10^{-31} T^6$
2c	$k_{vt,c}$	$\text{CO}_2^i(v_d, v_3) + \text{O} \rightleftharpoons \text{CO}_2^i(v_d', v_3 - 1) + \text{O}, \Delta v_d=2-4$	$2 \times 10^{-13} (T/300)^{1/2}$
3	$k_{vt,CO_2}$	$\text{CO}_2^i(v_d, v_3) + \text{CO}_2^i \rightleftharpoons \text{CO}_2^i(v_d + 1, v_3 - 1) + \text{CO}_2^i(v_d = 1)$	$3.6 \times 10^{-13} \exp(-1660 T + 176948/T^2)$
4	$k_{vv,O_2}$	$\text{CO}_2^i(v_d, v_3) + \text{O}_2 \rightleftharpoons \text{CO}_2^i(v_d + 1, v_3 - 1) + \text{O}_2(1)$	$3 \times 10^{-15}$
5a	$k_{vv,v_2}$	$\text{CO}_2^i(v_d) + \text{CO}_2^i \rightleftharpoons \text{CO}_2^i(v_d - 1) + \text{CO}_2^i(v_d = 1)$	$v_d \times 2.394 \times 10^{-11} \exp(-14.085 \Delta E/T)$
5b	$k_{vv,v_2,iso}$	$\text{CO}_2^i(v_d) + \text{CO}_2^j(v_d') \rightleftharpoons \text{CO}_2^i(v_d - 1) + \text{CO}_2^j(v_d' + 1)$	$i = 1, j = 2-4; 2.35 \times 10^{-11}$
6	$k_{vv}$	$\text{CO}_2(v_d, v_3) + \text{N}_2 \rightleftharpoons \text{CO}_2(v_d, v_3 - 1) + \text{N}_2(1)$	$5.0 \times 10^{-13} (300/T)^{0.5}$ for $v_d = 0, 1, 3, 5, 7$ $7.0 \times 10^{-13} (300/T)^{0.5}$ for $v_d = 2, 4, 6$
7a	$k_{F1}$	$\text{CO}_2(v_1, v_2', v_3) + \text{N}_2 \rightleftharpoons \text{CO}_2(v_1', v_2'', v_3) + \text{N}_2$	$5.4 \times 10^{-13}$ for $v_2 = v_2' = 0$ or $v_2$ and $v_2' \neq 0$
7b	$k_{F2}$	$\text{CO}_2(v_1, v_2', v_3) + \text{N}_2 \rightleftharpoons \text{CO}_2(v_1', v_2'', v_3) + \text{N}_2$	$8.1 \times 10^{-13}$ for all other cases
8	$k_{vv,iso}$	$\text{CO}_2^i(v_3) + \text{CO}_2^i(v_3') \rightleftharpoons \text{CO}_2^i(v_3 - 1) + \text{CO}_2^i(v_3' + 1)$	$i = 1; 6.8 \times 10^{-12} v_3 \sqrt{T}$ for $j = 1, 3-6$ $i = 1; 2.8 \times 10^{-12} v_3 \sqrt{T}$ for $j = 2$
9	$k_{O(^1D)}$	$\text{N}_2 + \text{O}(^1D) \rightarrow \text{N}_2(1) + \text{O}(^3P)$	$\epsilon \times 2.1 \times 10^{-11} \exp(115/T)$
10	$k_{OH}$	$\text{N}_2 + \text{OH}^*(v \leq 10) \rightarrow \text{N}_2(1) + \text{OH}^*(v - 1)$	$\epsilon = 0.2 \times 6.8 (N_2(1) \text{ per O}(^1D) \text{ molecule})$ $\epsilon \times (0.06, 0.1, 0.17, 0.3, 0.52, 0.91, 1.6, 11, 4.8, 6) \times 10^{-13}$ for $v = 1-10; \epsilon = 3.92 (N_2(1) \text{ per OH}(v) \text{ molecule})$
11	$k_{N_2,O_2}$	$\text{N}_2(1) + \text{O}_2 \rightleftharpoons \text{N}_2 + \text{O}_2$	$2.6 \times 10^{-19} + 5 \times 10^{-13} \exp(-73.9/T^{1/3})$
12	$k_{N_2,O}$	$\text{N}_2(1) + \text{O} \rightleftharpoons \text{N}_2 + \text{O}$	$3.2 \times 10^{-15} (T/300)^{2.9}$

<sup>†</sup>Rate coefficient for the forward sense of the process in cm<sup>3</sup>s<sup>-1</sup>. <sup>‡</sup>This rate is taken as 10<sup>-15</sup> cm<sup>3</sup>s<sup>-1</sup> for temperatures lower than 150 K (see text).  $T$  is temperature in K.  $i$  and  $j$  are different CO<sub>2</sub> isotopologues.  $i = 1-6$  except as noted.  $v_d=2v_1+v_2$ , e.g.,  $v_d=2$  is for the states (10002, 02201, 10001).

particularly for the CO<sub>2</sub>(01101) level, is still a major uncertainty in the calculation of its populations in the upper atmosphere and lower thermosphere. [García-Comas et al. \(2008\)](#) show a discrepancy of about a factor 4 between the rates measured in the laboratory and those deduced from atmospheric measurements. In this model, the value of  $6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K ([Sharma and Wintersteiner, 1990](#); [López-Puertas et al., 1992](#)) is adopted maintaining its temperature dependency:

$$k_{O,v_2=1 \rightarrow 0} = 3.5 \times 10^{-13} \sqrt{T} + 2.32 \times 10^{-9} \exp\left(\frac{-76.75}{T^{1/3}}\right). \quad (4.3)$$

The vibrational-vibrational (V-V) energy transfer of  $v_2$  quanta among the different CO<sub>2</sub> isotopologues has the following scheme:



where  $k_{vv,v_2}$  represents the V-V exchange for levels within a given isotope, and  $k_{vv,v_2,iso}$ , the exchange between two different isotopes.

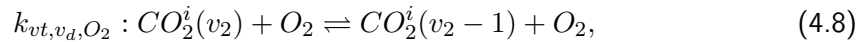
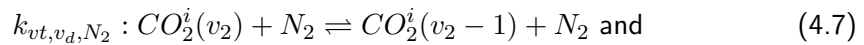
The exchange rate of  $v_2$  quanta in CO<sub>2</sub>-CO<sub>2</sub> V-V collisions has been updated by increasing it in a factor of two ([López-Puertas et al., 2009](#)). In addition, a new V-V  $v_2$  collisional scheme has been included based on the rate constants measured by [Dang et al. \(1983\)](#). The expressions for  $k_{vv,v_2}$  and  $k_{vv,v_2,iso}$  are

$$k_{vv,v_2} = v_d \times 2.394 \times 10^{-11} \exp\left(\frac{-9.788 c_2 \Delta E}{T}\right) \quad (4.5)$$

$$k_{vv,v_2,iso} = 2.35 \times 10^{-11}, \quad (4.6)$$

where  $c_2$  is the second radiative constant, 1.438777.

The processes of V-T collisional relaxation of CO<sub>2</sub>( $v_d, 0$ ) with N<sub>2</sub> and O<sub>2</sub> drives the populations of the  $v_d$  levels below and around the mesopause:



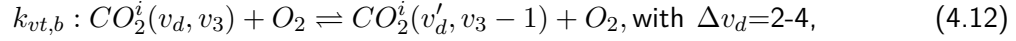
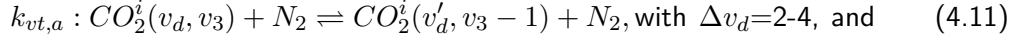
where the rates values are

$$k_{vt,v_d,N_2} = k \times 7 \times 10^{-17} \sqrt{T} + 6.7 \times 10^{-10} \exp\left(\frac{-83.8}{T^{1/3}}\right) \quad (4.9)$$

$$k_{vt,v_d,O_2} = k \times 7 \times 10^{-17} \sqrt{T} + 1.0 \times 10^{-9} \exp\left(\frac{-83.8}{T^{1/3}}\right), \quad (4.10)$$

with  $k = 1, 3, 4.5, 6.75, 9, 12$  for  $v_2 = 1, \dots, 6$  ([García-Comas et al., 2008](#)). Below 150 K no measurements were reported for these rates, and the extrapolated values from the fit of the measurements at higher temperatures resulted in very cold retrieved temperatures around the polar summer mesopause ([García-Comas et al., 2011](#)). For this reason, below 150 K, a constant value of  $10^{-15} \text{ cm}^3 \text{ s}^{-1}$  is assumed.

The scheme for the V-T relaxation of CO<sub>2</sub>(0,0<sup>0</sup>,1) in collisions with N<sub>2</sub> and O<sub>2</sub> is given by



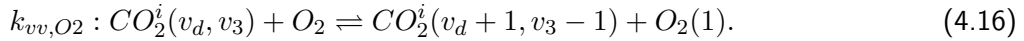
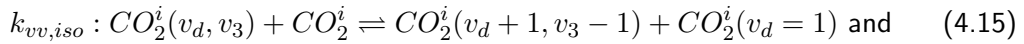
based on [Taine and Lepoutre \(1980\)](#) measurements. These processes have very important consequences for the population of CO<sub>2</sub>(0,0<sup>0</sup>,1) in the mesosphere. The rate values ([Inoue and Tsuchiya, 1975](#); [Rosser et al., 1969](#); [Rosser and Gerry, 1969](#); [Siddles et al., 1994](#)) are given by

$$k_{vt,a} = 1.10 \times 10^{-15} + 1.14 \times 10^{-10} \exp\left(-72.3/\sqrt[3]{T}\right) + 2.3 \times 10^{-40} T^9 \text{ and} \quad (4.13)$$

$$k_{vt,b} = 1.82 \times 10^{-15} + 3.10 \times 10^{-11} \exp\left(-63.3/\sqrt[3]{T}\right) + 2.0 \times 10^{-31} T^6. \quad (4.14)$$

Regarding the relaxation by O, the rate coefficient takes a value of  $k_{vt,c} = 2 \times 10^{-13} (T/300)^{0.5}$  ([López-Puertas et al., 1986b,a](#)).

The collisional process of the relaxation of CO<sub>2</sub>  $v_3$  to  $v_2$  quanta during collision with a ground state CO<sub>2</sub> molecule is of little importance in the Earth's atmosphere, although it is crucial for Mars and Venus. Regarding the relaxation of  $v_3$  to  $v_2$  by collisions with O<sub>2</sub>, it is not a significant producer of the CO<sub>2</sub> fundamental bending mode, but it is a significant loss mechanism for CO<sub>2</sub>(0,0<sup>0</sup>,1), and is important also for determining the populations of O<sub>2</sub>(1) and H<sub>2</sub>O(0,1<sup>1</sup>,0).

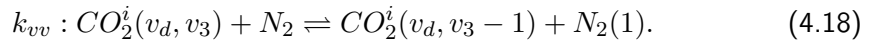


In the first case, the temperature dependency is given by ([Lepoutre et al., 1977](#))

$$k_{vv,iso} = 3.6 \times 10^{-13} \exp(-1660T + 176948/T^2), \quad (4.17)$$

and in the second case it takes the constant value of  $k_{vv,O_2} = 3 \times 10^{15}$  ([Alexander et al., 1968](#)).

The V-V coupling of CO<sub>2</sub>( $v_3$ ) with N<sub>2</sub> has the form of



These processes are of special interest in determining the populations of CO<sub>2</sub> isotopes, which significantly affected by the population of N<sub>2</sub>(1). Because of the infrared inactivity of N<sub>2</sub>(1), the energy absorbed from solar radiation by CO<sub>2</sub> in the near infrared (4.3 and 2.7 μm) is redistributed by these collisional processes among the ( $v_d, 1$ ) states of all CO<sub>2</sub> isotopes. In addition, it also takes into account the excitation of these levels from other non-LTE sources such as O(<sup>1</sup>D) and OH( $v \leq 10$ ), which previously excite N<sub>2</sub>(1). The temperature dependency is given by ([Inoue and Tsuchiya,](#)

1975; López-Puertas et al., 2005)

$$k_{vv} = 5.0 \times 10^{-13} (300/T)^{0.5} \text{ for } v_d = 0, 1, 3, 5, 7 \quad (4.19)$$

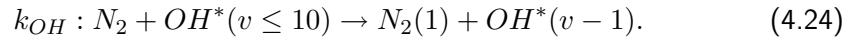
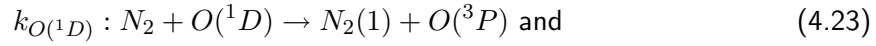
$$k_{vv} = 7.0 \times 10^{-13} (300/T)^{0.5} \text{ for } v_d = 2, 4, 6. \quad (4.20)$$

The relaxations within the CO<sub>2</sub> equivalent groups, i.e., all those levels having the same  $v_d$ , e.g. (10011, 10012, and 02211), sometimes called the Fermi coupled levels, are discussed in López-Puertas et al. (2005) and in more detail in Chapter 5. The solar pumping occurs only in allowed bands, but the exchange of energy between near-resonant high energy levels allows this energy to be re-emitted in other hot bands. These processes,  $k_{F1}$  and  $k_{F2}$  in Table 4.1, have rate coefficients of:

$$k_{F1} = 5.4 \times 10^{-13} \text{ for } v_2 = v'_2 = 0 \text{ or } v_2 \text{ and } v'_2 \neq 0; \quad (4.21)$$

$$k_{F2} = 8.1 \times 10^{-13} \text{ for all other cases.} \quad (4.22)$$

As we described before, the excitation of N<sub>2</sub> is very important due to the rapid V-V energy exchange between N<sub>2</sub>(1) and the CO<sub>2</sub>( $v_3$ ) levels. During daytime, the N<sub>2</sub> is excited from the collisions with electronically excited atomic oxygen, O(<sup>1</sup>D), and, at night, from the OH( $v \leq 10$ ) vibrationally excited levels:

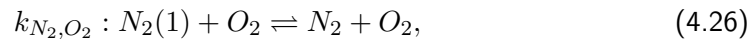


The value for the rate corresponding to O(<sup>1</sup>D) collisions is taken from Ravishankara et al. (2002),

$$k_{O(^1D)} = \epsilon \times 2.1 \times 10^{-11} \exp\left(\frac{115}{T}\right), \quad (4.25)$$

where  $\epsilon = 0.2 \times 6.8$  (N<sub>2</sub>(1) per O(<sup>1</sup>D) molecule). The rate coefficients for  $k_{OH}$  are  $k_{OH} = \epsilon \times (0.06, 0.1, 0.17, 0.3, 0.52, 0.91, 1.6, 11, 4.8, 6) \times 10^{-13}$  for  $v = 1-10$  (Adler-Golden, 1997); with  $\epsilon = 3.92$  (N<sub>2</sub>(1) molecules per OH( $v$ ) molecule) (López-Puertas et al., 2004).

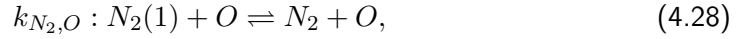
The quenching of N<sub>2</sub>(1) is mainly due to collisions with molecular and atomic oxygen. In the collisional process



part of the vibrational energy of N<sub>2</sub> is transferred to the O<sub>2</sub> molecule (being an important excitation mechanism of O<sub>2</sub>). The temperature dependency is given by (Gregory et al., 1983; Maricq et al., 1985)

$$k_{N_2, O_2} = 2.6 \times 10^{-19} + 5 \times 10^{-13} \exp\left(-\frac{73.9}{T^{1/3}}\right). \quad (4.27)$$

Regarding the  $N_2$  quenching process by collisions with atomic oxygen,



where the rate value is  $k_{N_2,O} = 3.2 \times 10^{-15} \exp(T/300)^{2.9}$  (Whitson and McNeal, 1977).

## 4.4. The Retrieval Control Program

The Retrieval Control Program, RCP, is a constrained least squares algorithm for retrieving the atmospheric parameters. RCP was conceived and developed at IMK with the non-LTE section implemented by the IAA team. The inputs to RCP are the initial guess and *a priori* information of the quantities to be retrieved, as well as the MIPAS level 1b measured spectra or, alternatively, spectra generated by KOPRA (or other similar forward model) when performing retrievals from synthetic spectra. These can be either calculated for LTE or for NLTE conditions with non-LTE populations calculated, e.g. by the GRANADA model.

Basically RCP solves iteratively the retrieval equation 3.53. The calculation of the model spectra and Jacobians is performed with KOPRA, being called in each step of the iteration. The measurement covariance matrix is calculated from the noise-equivalent spectral radiance provided with the L1b data. The regularization matrix is build from Tikhonov-type terms of different orders which can be combined to obtain a custom-tailored regularization for any particular retrieval problem. Alternatively, an externally generated regularization matrix can be read in. The RCP code uses, for stability, a Levenberg-Marquardt damping,  $\lambda I$ , (see Chapter 3, Sec. 3.5) which is forced to be zero in the last iteration. Convergence is reached when the change of the retrieval parameters with respect to the previous iteration is smaller than a certain fraction  $\epsilon$  of the expected noise retrieval error. All required control parameters such as the start value of  $\lambda I$ , or the convergence parameter  $\epsilon$  can be specified by the user in order to optimize the retrieval performance.

The principal output are the retrieved parameters but RCP can also provides diagnostics of the retrieval such as the averaging kernels, the noise error covariance matrix or the vertical resolution (see Section 3.5).

## 4.5. IMK-IAA non-LTE Retrieval Scheme

The combination of the three previously described codes, their interactions and the whole set of their respective inputs and outputs conform the IMK-IAA non-LTE retrieval scheme (see Fig.4.1).

This system was planned to improve the operational near-real time data processing developed by the European Space Agency (ESA) to process the MIPAS nominal mode data. The operational ESA retrieval scheme was designed to provide pressure,

temperature and volume mixing ratios of  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  within the first 3 hours after MIPAS spectra were taken (Ridolfi et al., 2000). The IMK-IAA retrieval scheme, in turn, is an offline scheme which can handle a larger number of species and in an extended altitude range, can be applied to all the MIPAS observational modes (including the middle and upper atmosphere modes), can handle non-LTE, and does not make a number of approximations which, in principle, make the retrievals more accurate.

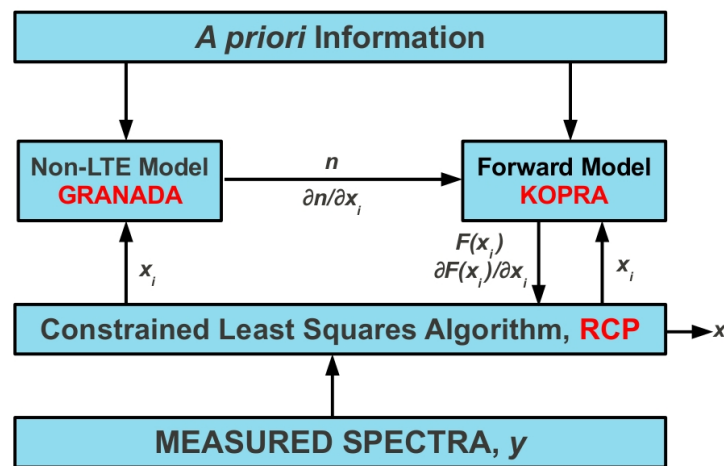


Figure 4.1: The IMK-IAA non-LTE retrieval scheme. The term  $x_i$  refers to the vector of the retrieval parameters within each iteration step,  $x$  to the output vector of retrieval parameter, and  $n$  to the non-LTE populations from GRANADA. KOPRA calculates the simulated spectra,  $F(x_i)$ , and the Jacobians,  $\partial F(x_i)/\partial x_i$  at each iteration.

In summary, the retrieval scheme works following these basic steps: i) the *a priori*<sup>2</sup> information is introduced in KOPRA and GRANADA; (ii) the latter performs the calculation of the non-LTE populations; (iii) KOPRA then takes the outputs from GRANADA for the calculation of the radiances and the Jacobians; (iv) the simulated spectra from KOPRA and the measured L1b MIPAS spectra (or synthetic spectra) are introduced in the constrained least squares algorithm, RCP, for iteration; (v) if the result does not satisfy the convergence criterion, the result is sent back to KOPRA and GRANADA for recalculation. Once the criterion is satisfied, the retrieved L2 data are finally obtained.

<sup>2</sup>In some cases the initial guess is used as *a priori*.



## Chapter 5

# Non-LTE Collisional Rates from MIPAS Data

### *Abstract*

In this chapter we present the retrieval of several vibrational-vibrational (V-V) and vibrational-thermal (V-T) collisional rate coefficients affecting the populations of the CO<sub>2</sub> levels emitting at 10, 4.3 and 2.7 μm from high resolution limb atmospheric spectra taken by MIPAS. The special characteristics of the MIPAS instrument (see Chapter 2) allows measuring the atmospheric limb emission in a wide altitude range, from 20 to 170 km in its middle and upper atmosphere modes, and hence obtain information on the temperature dependence of the collisional rates. In particular, the coefficients and their temperature dependence in the 130-250 K range of the following processes are retrieved: CO<sub>2</sub>(*v<sub>d</sub>*, *v<sub>3</sub>*) + N<sub>2</sub> ⇌ CO<sub>2</sub>(*v<sub>d</sub>*, *v<sub>3</sub>* - 1) + N<sub>2</sub>(1) with *v<sub>d</sub>* = 2*v<sub>1</sub>* + *v<sub>2</sub>* = 2, 3 and 4; CO<sub>2</sub>(*v<sub>1</sub>*, *v<sub>2</sub>*, *l*, 1, *r*) + M ⇌ CO<sub>2</sub>(*v'<sub>1</sub>*, *v'<sub>2</sub>*, *l'*, 1, *r'*) + M with Δ*v<sub>d</sub>* = *v'<sub>d</sub>* - *v<sub>d</sub>* = 0 and Δ*l* = 0; and with Δ*v<sub>d</sub>* = 0 and Δ*l* ≠ 0. In addition, we have also retrieved the thermal relaxation of CO<sub>2</sub>(*v<sub>3</sub>*) into the *v<sub>1</sub>* and *v<sub>2</sub>* modes, e.g., CO<sub>2</sub>(*v<sub>d</sub>*, *v<sub>3</sub>*) + M ⇌ CO<sub>2</sub>(*v'<sub>d</sub>*, *v<sub>3</sub>* - 1) + M with Δ*v<sub>d</sub>* = 2-4 and Δ*v<sub>3</sub>* = -1; and the efficiency of the excitation of N<sub>2</sub>(1) by O(<sup>1</sup>D). All of them were retrieved with a much better accuracy than were known before. The new rates have very important effects on the atmospheric limb radiance in the 10, 4.3 and 2.7 μm spectral regions (5-8% at 4.3 μm) and allow a more accurate inversion of the CO<sub>2</sub> volume mixing ratio in the mesosphere and lower thermosphere from measurements taken in those spectral regions. This work has been published in [Jurado-Navarro et al. \(2015c\)](#).

### 5.1. Introduction

As explained in Chapter 1, carbon dioxide, is an important greenhouse gas playing an essential role in the energy budget of the Earth's atmosphere. CO<sub>2</sub> originates strong atmospheric non-LTE (non Local Thermodynamic Equilibrium) infrared emission which is frequently use to infer its abundance in the middle/upper atmosphere.

The inversion of CO<sub>2</sub> abundances from atmospheric limb *emission* spectra requires, however, accurate and sophisticated modelling of the non-LTE populations of the states emitting at 10, 4.3 and 2.7 μm. These states are pumped by absorption of solar radiation, and are largely controlled by collisional vibrational-vibrational and

vibrational-thermal energy transfers to/from  $N_2$  (see Chapter 4 Section 4.3).

The rates of these V-V and V-T processes are, however, poorly known. Only a few of them have been measured in the laboratory and when so, measurements were done long time ago as, e.g. the V-V transfer rate between  $CO_2(00^0_1)$  and  $N_2(1)$  (Inoue and Tsuchiya, 1975). Sometimes they were also derived from atmospheric emission observations (Nebel et al., 1994) but with large uncertainties and assuming a reference background atmosphere because the atmospheric state was not measured simultaneously.

Thus one of the aims of this work is, by taking the advantage of MIPAS high spectral resolution, its high sensitivity and its wide spectral range, to improve our knowledge of the collisional processes governing the non-LTE populations of the  $CO_2$  levels emitting at 10, 4.3 and 2.7  $\mu m$ . To reach that objective we have retrieved rate coefficients for a number of collisional processes affecting to the  $CO_2$  states from MIPAS spectra. We describe in this chapter the methodology used and the results and conclusions obtained.

## 5.2. Retrieval Setup

As mentioned in Chapter 3, we have to make some a priori assumptions in order to stabilize the retrieval. The collisional rates are constrained to these a priori assumptions using a diagonal regularization matrix containing the related a priori variances, in the sense of maximum a posteriori (Rodgers, 2000). For the jointly fitted  $CO_2$  profile, a Tikhonov-type smoothing constraint (Tikhonov, 1963) is used together with a strong diagonal constraint below 70 km. The latter forces the retrieved  $CO_2$  in the stratosphere and lower mesosphere to be close to the well-known  $CO_2$  mixing ratio in the homosphere.  $CO_2$  a priori profiles have been taken from the Whole Atmosphere Community Climate Model with specified dynamics (SD-WACCM) simulations (Garcia et al., 2014) which is constrained with output from NASA's Modern-Era Retrospective Analysis (MERRA) (Rienecker et al., 2011) below approximately 1 hPa. Garcia et al. (2014) showed SD-WACCM simulations for Prandtl numbers ( $P_r$ ) of 4 (standard) and 2, corresponding to lower and higher eddy diffusion coefficients respectively. Here we used the simulations for  $P_r=2$ , which gives an overall better agreement with ACE CO and  $CO_2$ , with MIPAS CO (Garcia et al., 2014), as well as with the MIPAS  $CO_2$ , as shown in Chapter 6.

The retrievals are performed using selected spectral regions (micro-windows) in the 4.3 and 10  $\mu m$  regions which vary with tangent altitude in order to optimize computation time and minimize systematic errors (von Clarmann and Echle, 1998). In particular, error propagation due to horizontal inhomogeneities have been minimized by excluding opaque spectral lines which are insensitive to tangent point conditions.

In addition to the target retrieval variables, a height- and wavenumber-independent radiance offset and a continuum-like optical depth profile (below 60 km) are fitted jointly for each micro-window in order to compensate for offset calibration errors and spectrally smooth atmospheric contributions not reproduced by the radiative transfer

forward model.

To obtain the L2 data (retrieved quantities) from the L1b spectra, a sequence of preprocessing steps are required: i) Correction of the spectral shift, followed by the retrieval of temperature, horizontal temperature gradients, and elevation pointing from the 15  $\mu\text{m}$  spectral region (García-Comas et al., 2014); ii) extension of the retrieved temperature profile above 100 km with those retrieved from the spectrally resolved NO 5.3  $\mu\text{m}$  band (Bermejo-Pantaleón et al., 2011) and NRLMSIS-00 (Picone et al., 2002) above 170 km; iii) implicit determination of pressure by means of hydrostatic equilibrium (total density is obtained from pressure and temperature and using the ideal gas law); iv) retrieval of O<sub>3</sub> vmr (volume mixing ratio) from the 10  $\mu\text{m}$  spectral region (Gil-López et al., 2005); and v) generation of atomic oxygen O(<sup>3</sup>P) and O(<sup>1</sup>D) profiles below 100 km with a photochemical model (Funke et al., 2012) constrained by the O<sub>3</sub> and pressure/temperature data obtained in the previous steps. Above 100 km, we took the O<sub>2</sub> and the atomic oxygen concentrations from the NRLMSIS-00 model, and also use the same photochemical model for the calculation of O(<sup>1</sup>D) from the O<sub>2</sub> photodissociation (O<sub>3</sub> is not required in this region).

### 5.3. Microwindow Selection

The retrievals are performed from selected spectral regions which vary with tangent altitudes in order to optimize computation time, minimize systematic errors, and to avoid saturated spectral lines. The information coming from the CO<sub>2</sub> fundamental, first, second, third and fourth hot band emissions is mainly measured by the MIPAS channel D (1820-2410 cm<sup>-1</sup>) near the 4.3  $\mu\text{m}$  region. Additional information about the non-LTE population of the (00011) state, responsible for the 4.3  $\mu\text{m}$  fundamental band, comes from the CO<sub>2</sub> laser bands measured by the MIPAS channels A (685-970 cm<sup>-1</sup>) and AB (1020-1170 cm<sup>-1</sup>) respectively near 10  $\mu\text{m}$  (Jurado-Navarro et al., 2012, 2013). In order to obtain the information from all of these CO<sub>2</sub> bands, we used an extended set of 24 microwindows (MWs) covering these three channels. Considered spectral points within these MWs, vary with tangent height. That is, within each MW, a height-dependent mask of “sub-microwindows” is defined.

In this work we use the MIPAS spectra taken in its upper atmosphere observation mode (UA) from 40 km to 172 km (from high stratosphere to lower thermosphere including the mesosphere). Within these altitudes the non-LTE unsaturated lines gives an optimal sensitivity to the collisional rates involved in the retrieval with a good signal-to-noise ratio up to about 142 km.

The set of sub-microwindows was selected by analyzing the information in the calculated CO<sub>2</sub> vmr Jacobians, i.e. testing the sensitivity of the radiance to CO<sub>2</sub> vmr changes ( $\partial\mathbf{F}(C\vec{O}_2)/\partial C\vec{O}_2$ ). This useful tool allows us to discriminate the lines with a local response from those opaque and saturated at any given tangent height. The Jacobians were computed using the GRANADA model (Sec. 4.2) and the KOPRA code (Sec. 4.1) for a typical mid-latitude reference atmosphere (April, 45°N) (see Funke et al., 2012).

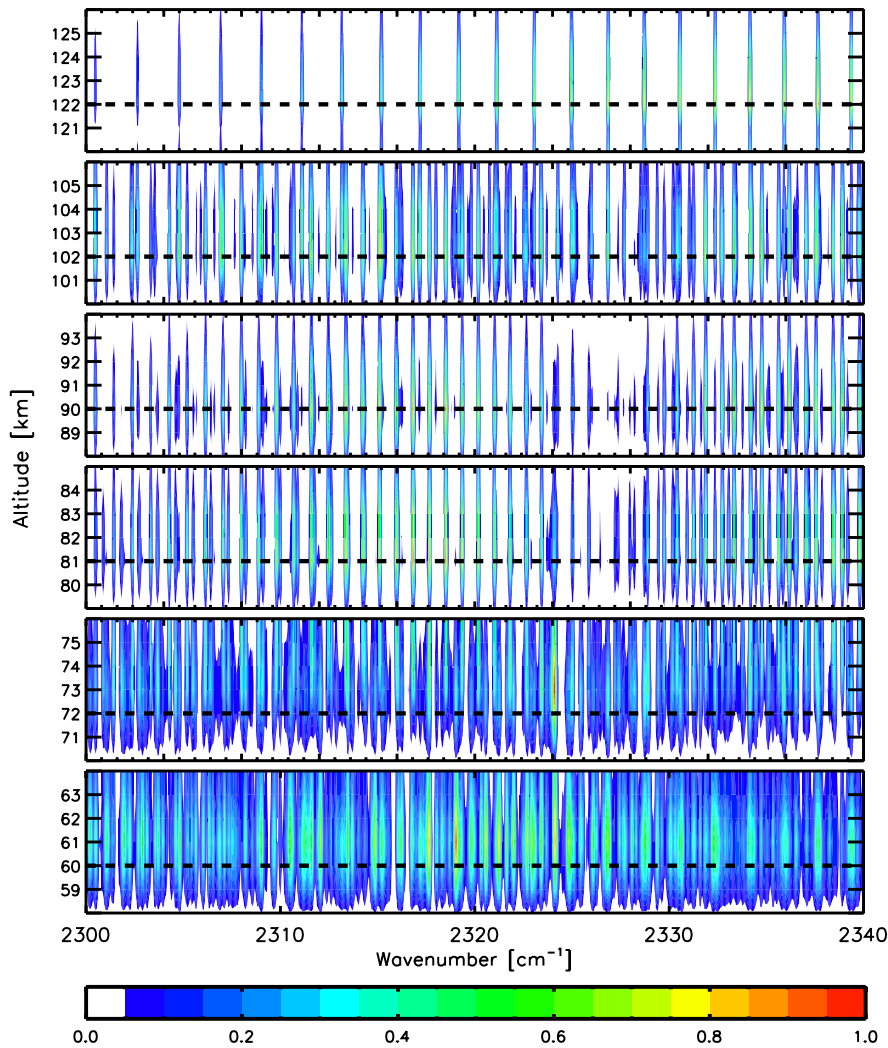


Figure 5.1: CO<sub>2</sub> Jacobians in the range 2300-2340 cm<sup>-1</sup> for 5 tangent heights (60, 72, 81, 90 and 102 km). The Jacobians are normalized to the tangent height maximum value. The coolest colours indicates poor sensitivity and the warmest ones high sensitivity, white regions shows no sensitivity. Black dashed lines indicate the tangent height for each case.

Analysing the Jacobians in the 4.3  $\mu\text{m}$  region (Figs. 5.1 and 5.2), we find that tangent heights from 60 to 81 km and above 102 km are mainly sensitive to the fundamental band lines while the second hot band contributes most in the altitude region from 84 to 102 km. The 2300-2340 cm<sup>-1</sup> range (Fig. 5.1) includes the P branch of the fundamental band and the 2340 to 2380 cm<sup>-1</sup> region (Fig. 5.2) includes its R branch. The P 16e (2335.9194 cm<sup>-1</sup>) and the R 16e (2361.4660 cm<sup>-1</sup>) are the strongest fundamental band lines in the 4.3  $\mu\text{m}$  region. On the other hand, the second hot band has its P branch located from 2300 to 2325 cm<sup>-1</sup> and the R branch in the 2330-2355 cm<sup>-1</sup> range. As we know, the second hot band is constituted by 3 vibrational transitions, the most intense is  $10^0_1 \rightarrow 10^0_0$ , having its strongest lines at

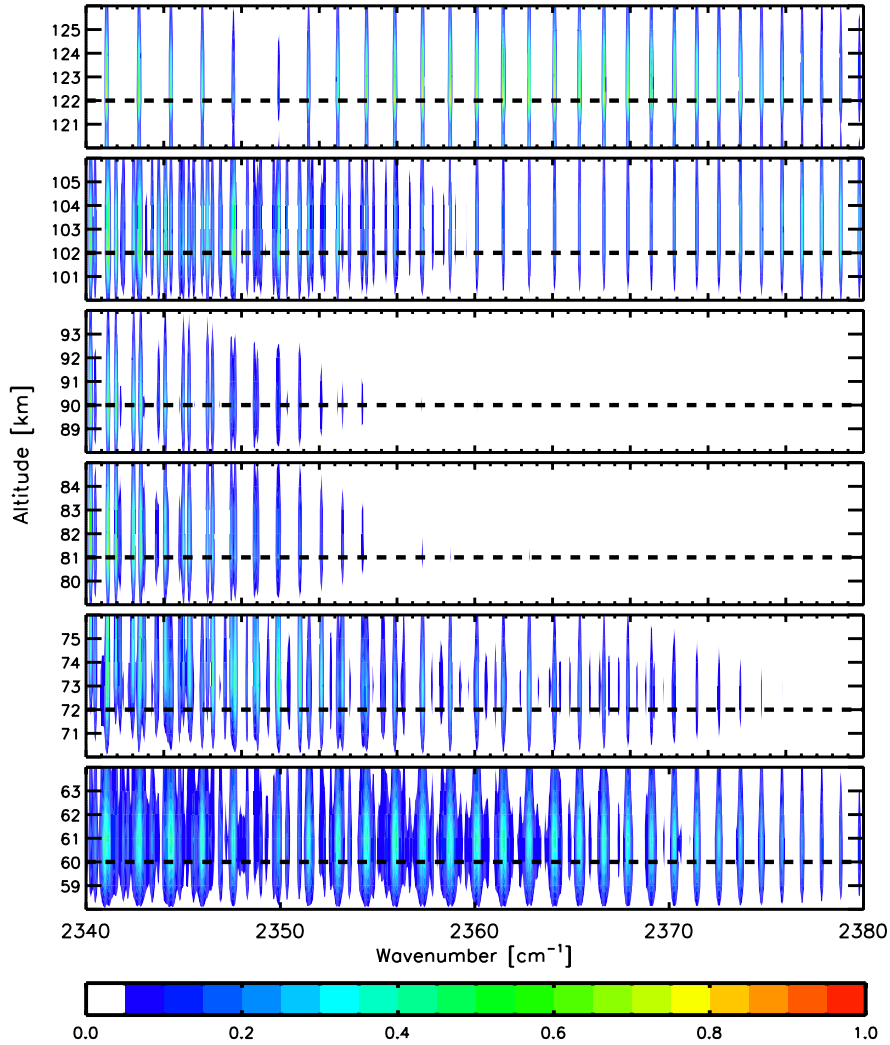


Figure 5.2: As Figure 5.1 but for the Jacobians in the range of 2340-2380  $\text{cm}^{-1}$ .

2314.2246  $\text{cm}^{-1}$  (P 16e) and at 2339.7941  $\text{cm}^{-1}$  (R 16e).

Regarding the Jacobians in the 10  $\mu\text{m}$ , sensitive lines of the transition  $00^0_1 \rightarrow 10^0_0$  are found at 925-970  $\text{cm}^{-1}$  (see Fig. 5.3) with the P16e and R16e lines at 947.7420  $\text{cm}^{-1}$  and 973.2885  $\text{cm}^{-1}$ , respectively, being the strongest ones. Those of the  $00^0_1 \rightarrow 02^0_0$  band are located at 1020-1080  $\text{cm}^{-1}$  (see Fig. 5.4) with the most intense lines P16e and R16e at 1050.4413  $\text{cm}^{-1}$  and 1075.9878  $\text{cm}^{-1}$ , respectively.

Spectral lines with strong non-local responses are mainly found in the fundamental and second hot bands at 4.3  $\mu\text{m}$ . These lines are excluded from the MW selection at a given tangent height whenever the value of the Jacobian 5 km above this tangent height exceeds 40% of the value at the tangent height, or if its value 15 km above the tangent height is higher than 5%. This selection criterium warranties that we obtain information close to the tangent height at work, i.e. avoiding Jacobians with high values at altitudes well above the tangent height (long tails).

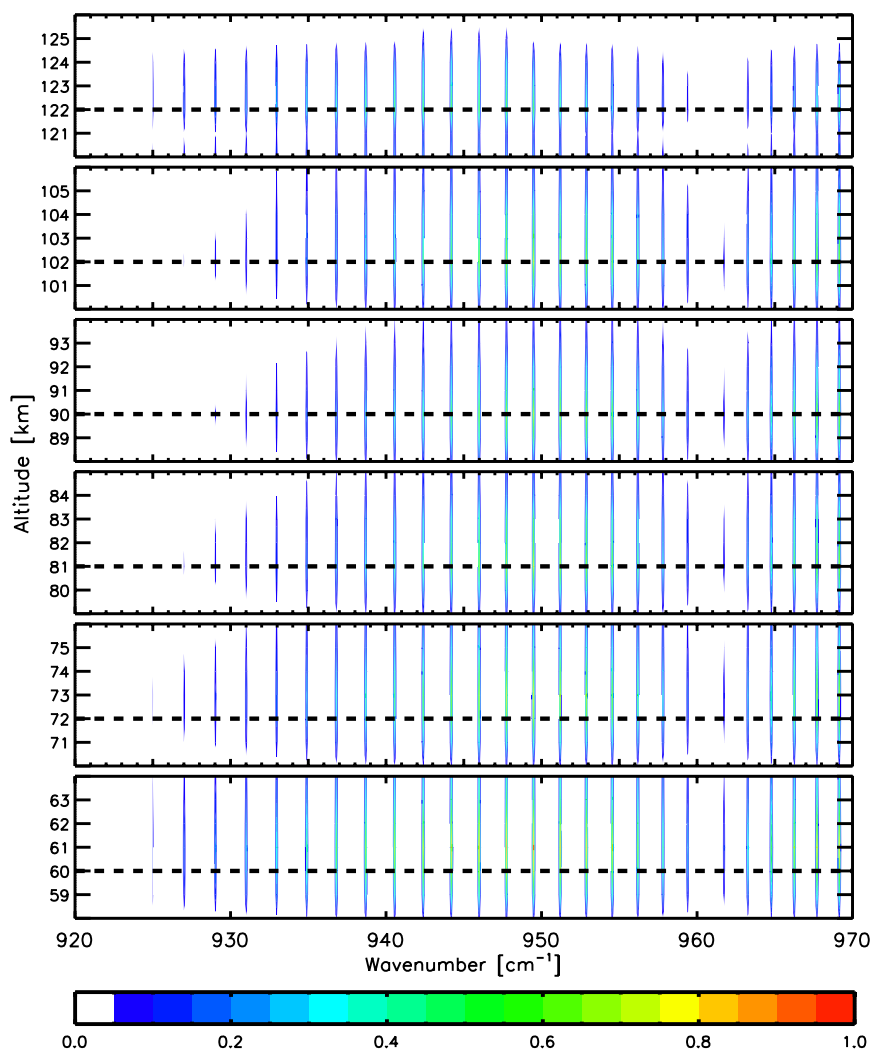


Figure 5.3: As Figure 5.1 but for the Jacobians in the range of 920-970  $\text{cm}^{-1}$ .

In principle, only the stronger lines with high sensitivity should be considered in the MWs in order to optimize computation time. However, the Jacobians used in the MW selection were calculated only for the  $\text{CO}_2$  vmr while our retrieval requires independent information on both  $\text{CO}_2$  and collisional parameters. Therefore, broad sub-microwindows, including unsaturated spectral lines of a large variety of vibrational bands, have been added above 66 km in the  $4.3 \mu\text{m}$  region in order to ensure independent information on both, the non-LTE collisional rates and the  $\text{CO}_2$  abundance. The resulting height-dependent mask of sub-microwindows (also called occupation matrix) is shown in Figs 5.5 and 5.6.

Due to the need to consider broad sub-microwindows in the  $4.3 \mu\text{m}$  region, the processor had to handle with heavy calculations. For this reason, the collisional rate retrieval had to be restricted to only for 4 representative days in 2010, 2 in solstice (17 January and 8 June) and 2 in equinox (30 March and 26 September).

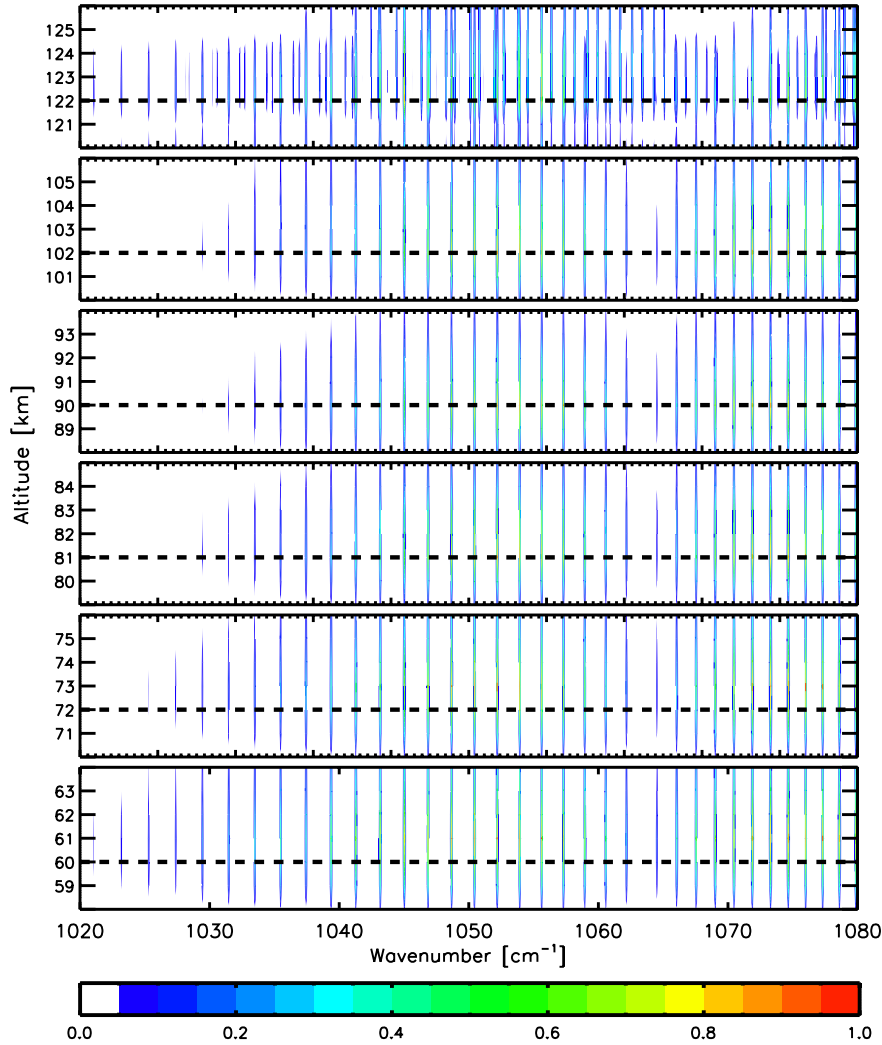


Figure 5.4: As Figure 5.1 but for the Jacobians in the range of 1020-1080  $\text{cm}^{-1}$ .

## 5.4. Sensitivity of Non-LTE Populations and 4.3 $\mu\text{m}$ Radiance to Collisional Rates

In Chapter 4, Sec 4.2, we described the non-LTE modelling of GRANADA including all collisional processes that control the populations of the  $\text{CO}_2$  vibrational levels. Here, we have carried out sensitivity studies for the most important rate coefficients that control their populations in order to find out which of them will be retrievable from MIPAS spectra.

Table 5.1 is an extract of Table 4.1 showing the processes we have analyzed in detail, or that we have retrieved. Also, Figs. 5.7a-c show diagrams where we visualized the vibrational states connected by those collisional processes. We refer here to Sec. 4.3, where we explain the different notations used for the  $\text{CO}_2$  vibrational states. Table A.1 is useful in this respect, since it shows the correspondence between



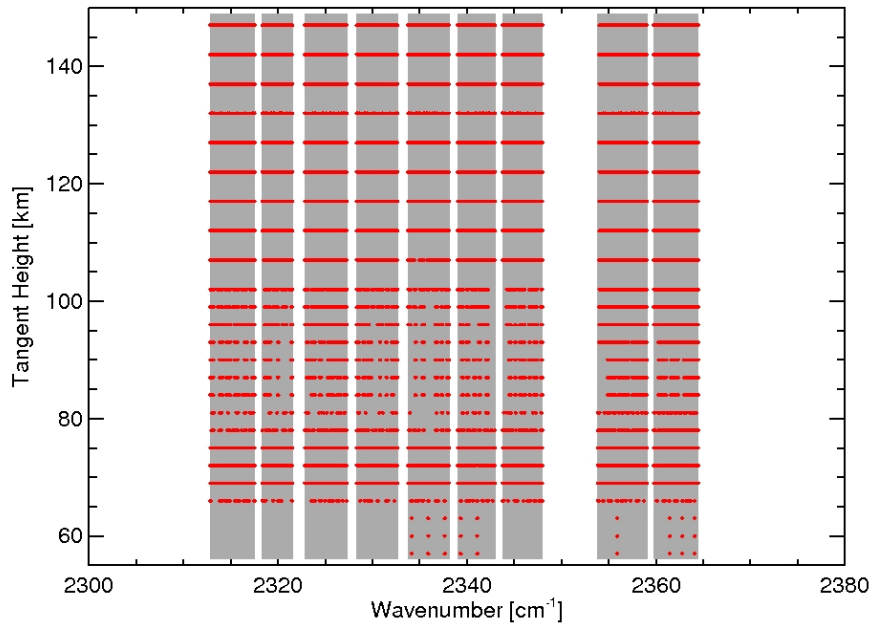


Figure 5.5: Occupation matrix of the joint retrieval of the rate coefficients and CO<sub>2</sub> vmr in 4.3 μm region. Shaded regions represent the micro-windows selected and red dots the sub-micro-window masks at each tangent height.

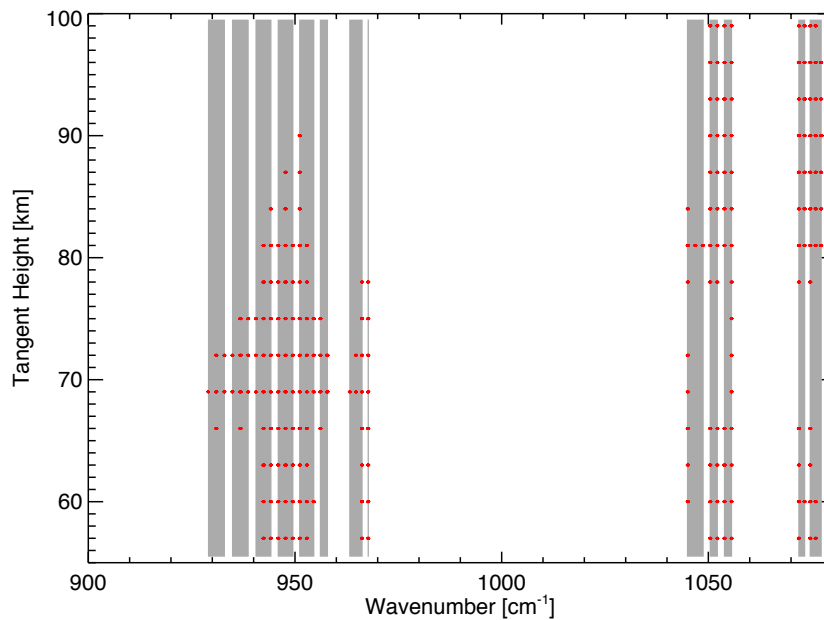


Figure 5.6: As Figure 5.5 but for the 10 μm region.

the two notations for most of the levels studied here.

Figures 5.8 and 5.9 show the vibrational temperature response of the main vibrational levels emitting at 4.3 μm (00011, 01111, 10011, 10012, and 02211 of the major



Table 5.1: Energy transfer processes studied in this work.

No.	Rate	Process	Rate coefficient (cm <sup>3</sup> s <sup>-1</sup> ) (previous works)	k <sub>0</sub> <sup>‡</sup>	Rate (this work) α <sup>‡</sup>
1	k <sub>vv0</sub>	CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> ) <sup>†</sup> +N <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> -1)+N <sub>2</sub> (1), v <sub>d</sub> =0	5.0·10 <sup>-13</sup> √300/T	4.64*	0.64*
2	k <sub>vv1</sub>	CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> )+N <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> -1)+N <sub>2</sub> (1), v <sub>d</sub> =1	5.0·10 <sup>-13</sup> √300/T	4.64*	0.64*
3	k <sub>vv2</sub>	CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> )+N <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> -1)+N <sub>2</sub> (1), v <sub>d</sub> =2	5.0·10 <sup>-13</sup> √300/T	5.02±0.22	1.0
4	k <sub>vv3</sub>	CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> )+N <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> -1)+N <sub>2</sub> (1), v <sub>d</sub> =3	5.0·10 <sup>-13</sup> √300/T	5.61±0.22	0.6
5	k <sub>vv4</sub>	CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> )+N <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> -1)+N <sub>2</sub> (1), v <sub>d</sub> =4	5.0·10 <sup>-13</sup> √300/T	5.64±0.09	0.6
6	k <sub>FF1</sub>	CO <sub>2</sub> (v <sub>1</sub> , v <sub>2</sub> <sup>b</sup> , 1)+M ⇌ CO <sub>2</sub> (v <sub>1</sub> <sup>b</sup> , v <sub>2</sub> <sup>b</sup> , 1)+M Δv <sub>d</sub> =0, Δl≠0	1.5·10 <sup>-13</sup> -3·10 <sup>-11</sup>	7.04±0.33	0.0
7	k <sub>FF2</sub>	e.g., CO <sub>2</sub> (1, 0 <sup>0</sup> , 1)+M ⇌ CO <sub>2</sub> (0, 2 <sup>0</sup> , 1)+M CO <sub>2</sub> (v <sub>1</sub> , v <sub>2</sub> <sup>b</sup> , 1)+M ⇌ CO <sub>2</sub> (v <sub>1</sub> <sup>b</sup> , v <sub>2</sub> <sup>b</sup> , 1)+M Δv <sub>d</sub> ≠0, Δl≠0	1.5·10 <sup>-13</sup> -2.4·10 <sup>-12</sup>	5.57±0.20	1.2
8a	k <sub>FF2'</sub> k <sub>vt,a</sub>	e.g., CO <sub>2</sub> (0, 2 <sup>2</sup> , 1) + M ⇌ CO <sub>2</sub> (0, 2 <sup>0</sup> , 1) + M, or CO <sub>2</sub> (1, 0 <sup>0</sup> , 1) + M ⇌ CO <sub>2</sub> (0, 2 <sup>2</sup> , 1) + M CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> )+N <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> <sup>b</sup> , v <sub>3</sub> -1)+N <sub>2</sub>	3·10 <sup>-13</sup> -4.8·10 <sup>-12</sup> f · [1.10·10 <sup>-15</sup> + 1.14·10 <sup>-10</sup> exp(-72.3/√T)]*	5.57±0.20 f=0.7±0.13	1.2
8b	k <sub>vt,b</sub>	Δv <sub>d</sub> =2-4 CO <sub>2</sub> (v <sub>d</sub> , v <sub>3</sub> )+O <sub>2</sub> ⇌ CO <sub>2</sub> (v <sub>d</sub> <sup>b</sup> , v <sub>3</sub> -1)+O <sub>2</sub>	f · [1.82·10 <sup>-15</sup> + 3.10·10 <sup>-11</sup> exp(-63.3/√T)]*	f=0.7±0.13	
9	k <sub>O(1D)</sub>	Δv <sub>d</sub> =2-4 N <sub>2</sub> + O(1D) → N <sub>2</sub> (1) + O	f · ε · 2.1·10 <sup>-11</sup> exp(115/T)* ε=0.2×6.8	f=1±0.15	
10	k <sub>N<sub>2</sub>,O</sub>	N <sub>2</sub> (1) + O(3P) → N <sub>2</sub> + O	4.5·10 <sup>-15</sup> (T/300) <sup>1.5</sup>		

(<sup>†</sup>) v<sub>d</sub> = 2v<sub>1</sub> + v<sub>2</sub>. (<sup>‡</sup>) k<sub>0</sub> with estimated total errors (in units of 10<sup>-13</sup> cm<sup>3</sup>s<sup>-1</sup>) (see Table 5.2) and α as in k = k<sub>0</sub> (300/T)<sup>α</sup>. \*Used (not retrieved) in this work. \* f is equal to 1 in previous works.

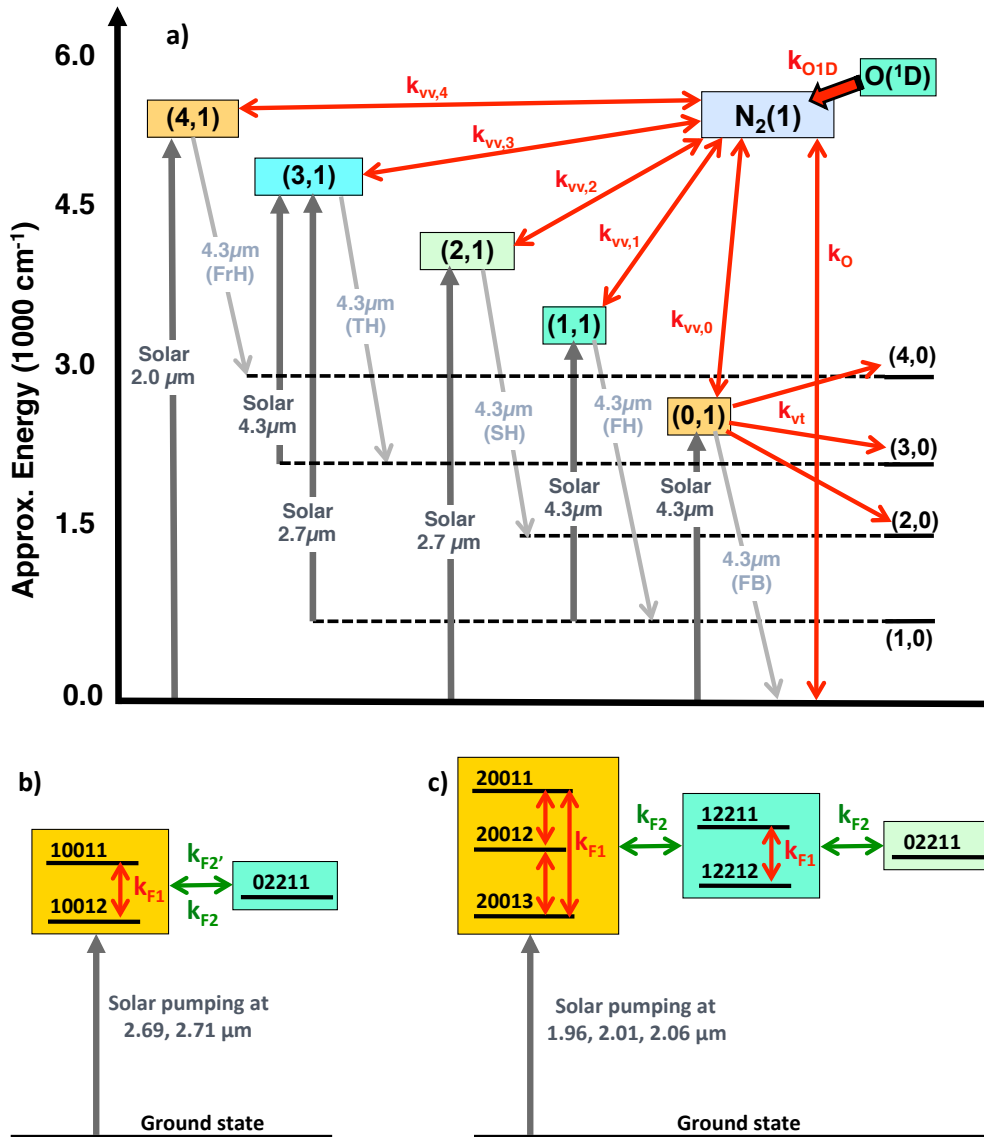


Figure 5.7: Schematic diagram showing the collisional rates  $k_{vv}$  considered in this work (see Table 5.1). Panel a) shows (in red) the processes  $k_{vv,0}$ ,  $k_{vv,1}$ ,  $k_{vv,2}$ ,  $k_{vv,3}$ ,  $k_{vv,4}$ ,  $k_{vt}$ , and  $k_{O(^1D)}$  of the major CO<sub>2</sub> isotopologue. The deactivation of N<sub>2</sub>(1) by O(<sup>3</sup>P),  $k_{N_2,O}$ , is also shown. The energy levels follow the  $(v_d, v_3)$  notation with  $v_d = 2v_1 + v_2$ . N<sub>2</sub>(1) and O(<sup>1</sup>D) energy levels are not at scale. Panels b) and c) show the  $k_{F1}$  (in red) and  $k_{F2}$  (in green) processes for the  $(v_d=2, v_3=1)$  and  $(v_d=4, v_3=1)$  levels, respectively.  $k_{F2'}$  and  $k_{F2}$  in panel b) correspond to the processes between (10011–02211) and (10012–02211), respectively.

isotopologue, and 00011 of the second one) to 10% changes in the collisional rates  $k_{vv,0}$ ,  $k_{vv,1}$ ,  $k_{vv,2}$ ,  $k_{F1}$ ,  $k_{F2}$ , and  $k_{vt}$  (see Table 5.1 and Fig. 5.7a). The responses of these populations to 10% changes in the  $k_{vv,3}$  and  $k_{vv,4}$  rates are very small and are not shown. As we expect the response to be dependent on the temperature profile,

the sensitivity has been performed for typical, i.e., mid-latitudes, as well as extreme, polar summer- and polar winter-like, temperature profiles.

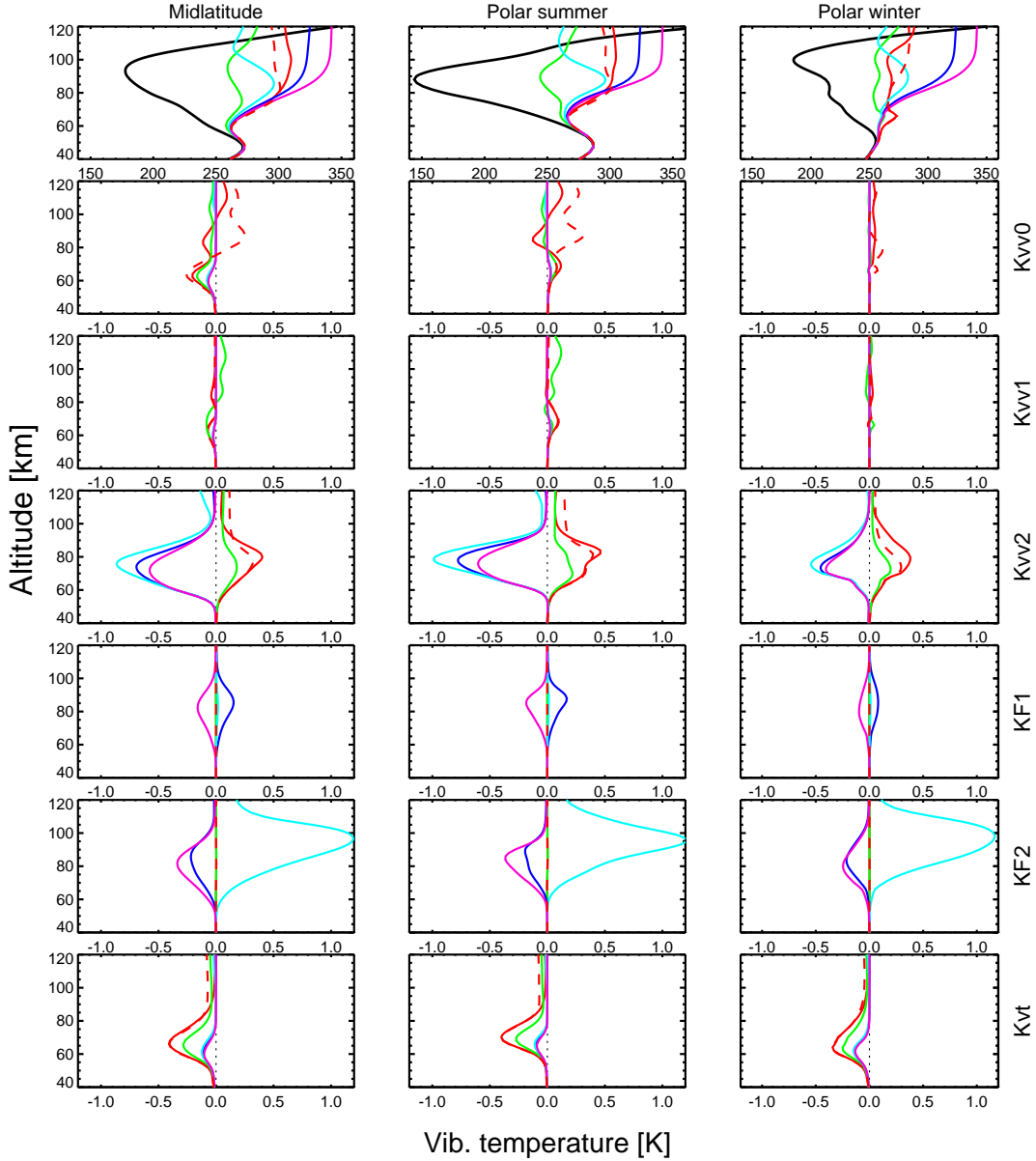


Figure 5.8: Sensitivity of the populations of the CO<sub>2</sub> levels 00011 (red solid: isotopologue 626, red dashed: isotopologue 636), 01111 (green), 10012 (dark blue), 02211 (light blue), and 10011 (magenta) to a 10% increase of the collisional rate constants for mid-latitude (left), polar summer (middle) and polar winter (right) conditions. From top to bottom: nominal vibrational temperatures; vibrational temperature changes due to an increase of  $k_{vv,0}$ ,  $k_{vv,1}$ ,  $k_{vv,2}$ ,  $k_{F1}$ ,  $k_{F2}$ , and  $k_{vt}$  (see Table 5.1). The temperature profiles and reference atmospheres were taken from the case of April at 45°N (solar zenith angle of 44.5°) of Funke et al. (2012).

We see that there is a weak sensitivity to changes in  $k_{vv,0}$  and particularly in  $k_{vv,1}$

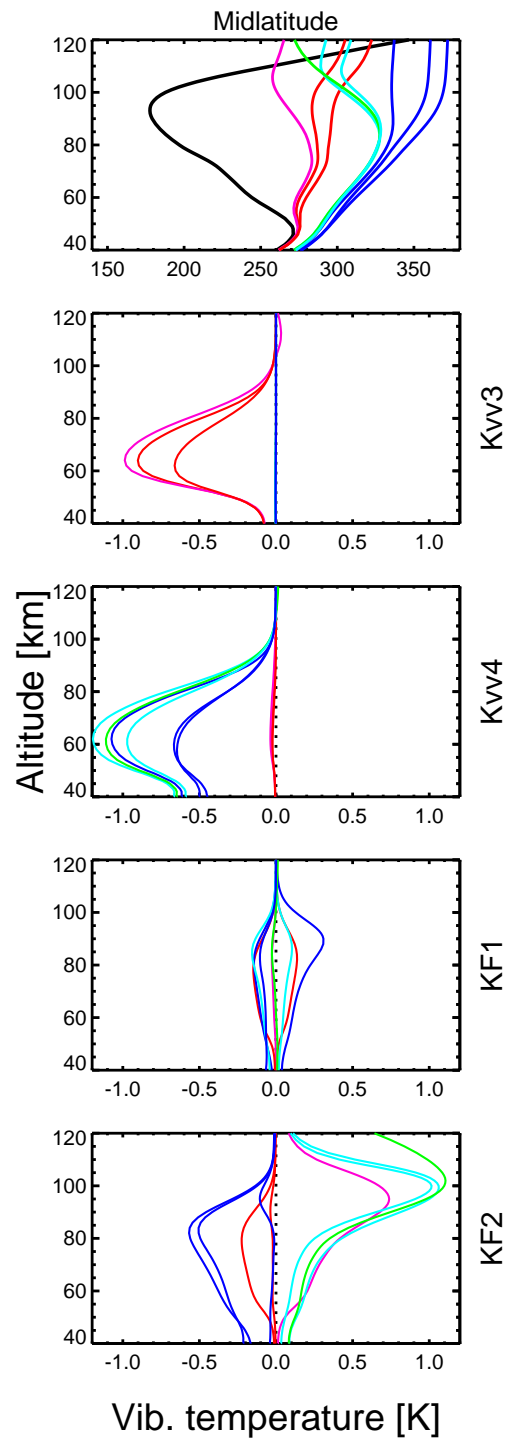


Figure 5.9: Sensitivity of the populations of the CO<sub>2</sub> levels 03311 (magenta), 1111f (red), 04411 (green), 1221f (light blue), and 2001f (dark blue) to a 10% increase of the collisional rate constants for midlatitude conditions. From top to bottom: nominal vibrational temperatures; vibrational temperature changes to due increases of  $k_{vv3}$ ,  $k_{vv4}$ ,  $k_{F1}$ , and  $k_{F2}$ .

(lower than 0.2 K) but a significant response to changes of  $k_{vv,2}$ ,  $k_{F1}$ ,  $k_{F2}$ , and  $k_{vt}$ . The response to  $k_{vv,2}$  is particularly significant. The increase of this rate by 10% leads to a significant depletion of the populations of the 2.7  $\mu\text{m}$  levels (10012, 02211 and 10011) and a simultaneous enhancement in the populations of the 00011 level of the two major isotopologues as well as that of 01111. Further, the response is found over a large altitude region, covering 50 to 95 km. As expected, the response is smaller for polar winter conditions when the mesospheric temperature is larger and more isothermal.

This large and altitude-extended response is very important since it would allow us to derive this rate accurately for different atmospheric conditions and therefore to gain information about its temperature dependence (Jurado-Navarro et al., 2015a, 2013). The response to the changes of the rates in the  $\text{CO}_2$  limb spectral radiance as would be measured by MIPAS are shown in Figures 5.10 and 5.11 for tangent heights of 60 and 80 km, respectively. The effect of perturbing  $k_{vv,0}$  and  $k_{vv,1}$  is very small,  $\leq 0.2 \text{ nW}/(\text{cm}^2 \text{ sr cm}^{-1})$ . This is about a factor of 15 smaller than the NESR (Noise Equivalent Spectral Radiance) of MIPAS in band D ( $1820\text{-}2410 \text{ cm}^{-1}$ ) of  $3 \text{ nW}/(\text{cm}^2 \text{ sr cm}^{-1})$ . Hence, the retrieval of these rates from single MIPAS spectra (as we have performed for the other rates) would be very difficult and unstable. Therefore we have not attempted to retrieve them.

On the other hand, the spectra clearly show the decrease of the emission from the 4.3  $\mu\text{m}$  second hot bands when perturbing  $k_{vv,2}$  for both tangent heights. These changes amount up to  $3 \text{ nW}/(\text{cm}^2 \text{ sr cm}^{-1})$  at 60 km and  $4.5 \text{ nW}/(\text{cm}^2 \text{ sr cm}^{-1})$  at 80 km.

The effects of perturbing  $k_{vv,2}$  on the emission of the 4.3  $\mu\text{m}$  fundamental is much smaller ( $\sim 0.5 \text{ nW}/(\text{cm}^2 \text{ sr cm}^{-1})$ ), and of opposite sign, but perceptible at a tangent height of 60 km (see the fourth panel of Figure 5.10).

The effects of perturbing the rates affecting the redistribution of energy among the solar pumped levels ( $k_{F1}$ ) and between these and the adjacent non-pumped levels ( $k_{F2}$ ) (see Table 5.1 and Figs. 5.7b and 5.7c) are shown in Figure 5.8 (5th and 6th rows) for the levels pumped by solar radiation in the 2.7  $\mu\text{m}$  fundamental bands and in Figure 5.9 (4th and 5th panels) for the higher levels pumped by solar radiation in the 2.7  $\mu\text{m}$  first hot bands and in the 2.0  $\mu\text{m}$  bands. As expected,  $k_{F1}$  perturbs only the solar-pumped levels, increasing the population of the more weakly pumped level, 10012, at the expense of the more excited 10011 state. Vibrational populations are affected by these processes between 60 km and 100 km. Similarly, increasing the rate of the collisional coupling of the solar-pumped to the non-excited levels, depletes the populations of the former in favor of the latter. The enhancement of the non-pumped level is very large, extending to higher altitudes due to the absorption of upwelling radiation in the 4.3  $\mu\text{m}$  hot band. We see similar effects in the higher energy levels in Fig. 5.9 (4th and 5th panels). All of these levels emit in the 4.3  $\mu\text{m}$  region, generating the second (SH), third (TH) and fourth (FrH) hot bands (see Table A.1). The effects of the perturbations of these rates on the spectra as measured by MIPAS are shown in Figs. 5.10 and 5.11 (two bottom panels). We see that there is a significant change in the spectral radiance at both tangent altitudes, between about

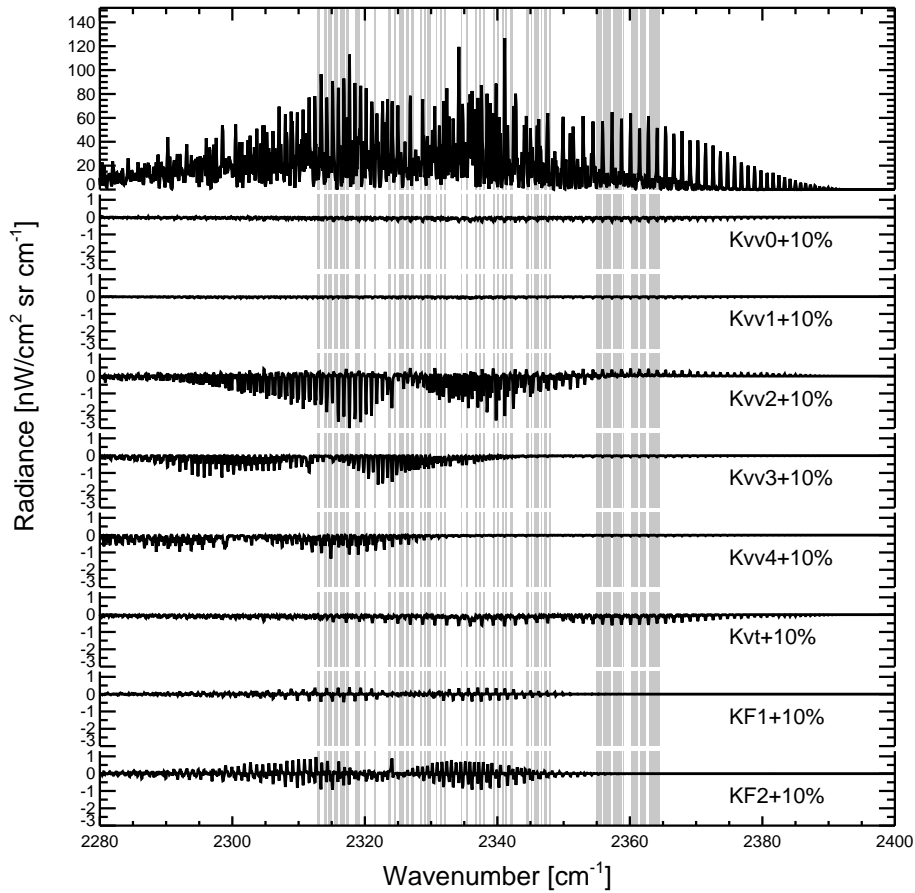


Figure 5.10: Sensitivity of CO<sub>2</sub> limb spectral radiances (tangent height of 60 km) as would be measured by MIPAS to a 10% increase of the collisional rate constants for midlatitude conditions (see Figs. 5.8 and 5.9). From top to bottom: simulated radiances; radiances changes to due an increase of  $k_{vv0}$ ,  $k_{vv1}$ ,  $k_{vv2}$ ,  $k_{vv3}$ ,  $k_{vv4}$ ,  $k_{vt}$ ,  $k_{F1}$ , and  $k_{F2}$ . Grey shaded regions indicate the spectral regions (micro-windows) used in the retrieval of the rates.

1.5 and 3.5 nW/(cm<sup>2</sup> sr cm<sup>-1</sup>). The perturbations are more important at 80 km and  $k_{F2}$  shows a larger response.

The response of the population of the levels to the collisional rates  $k_{vv,3}$  and  $k_{vv,4}$  (see Table 5.1) are shown in Fig. 5.9 (2nd and 3rd panels). We see that only the more energetic levels directly affected by these rates are significantly perturbed while the populations of 00011, of the 2.7  $\mu\text{m}$  levels, and of N<sub>2</sub>(1) (not shown) are hardly modified. That is important since the spectral lines of the bands originating from these levels will give us information on these rates, with no significant cross-talk to other rate coefficients. It is also noticeable that the sensitivity region is lower than for other rates, with a peak at around 60 km and significant down to as far as 40 km. The levels directly affected by these rates generate the third and fourth hot bands near 4.3  $\mu\text{m}$  (see Table A.1). The mapping of the changes in their populations into the spectra are shown in Figs. 5.10 and 5.11 (5th and 6th panels) for 60 km and 80 km, respectively. They are significant, particularly at the 60 km tangent height.

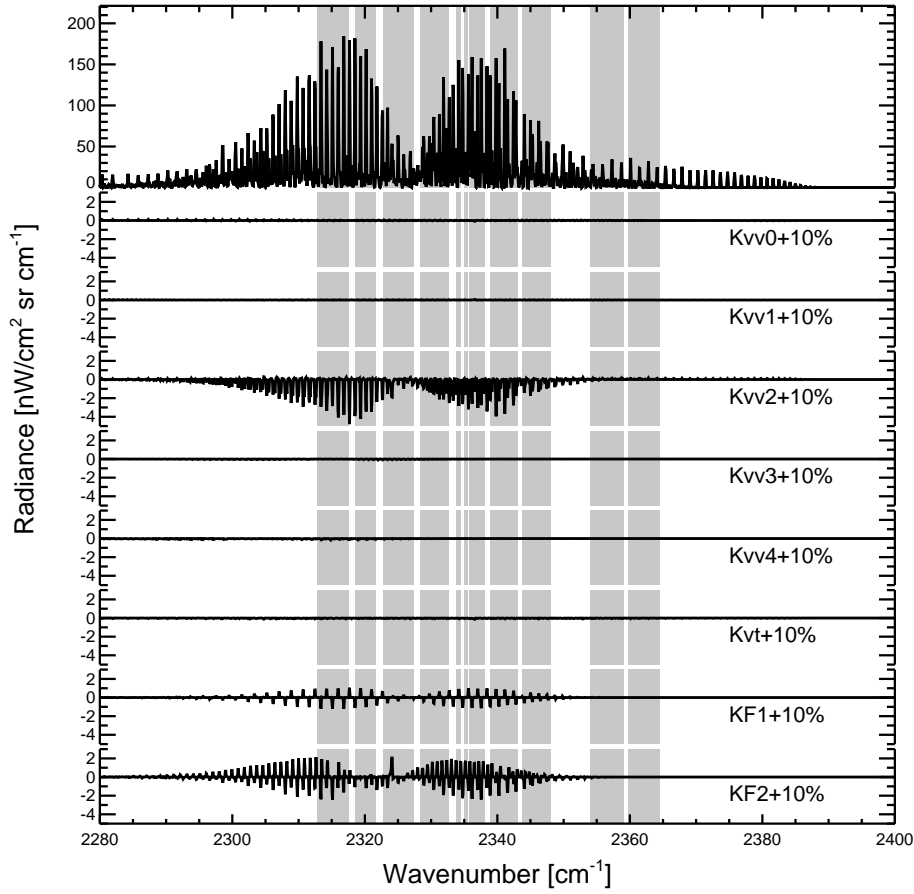


Figure 5.11: As Fig. 5.10, but for a tangent height of 80 km.

The sensitivity of the levels populations to  $k_{vt}$  is shown in Fig. 5.8, bottom row. As expected, when the rate increases, the population of 00011 significantly decreases. All other energy levels hardly change, except 01111, which is also significantly depopulated. Although the region of the change of the population of 00011 to this rate is slightly overlapping with that of  $k_{vv,2}$  (4th row), they are very clearly distinguishable and hence, the emission from this energy level will provide independent information on the two parameters. The effects on simulated MIPAS spectra are shown in Figs. 5.10 and 5.11 (7th panel). We observe here that the major information comes from tangent heights closer to 60 km rather than 80 km.

In summary, we have demonstrated that MIPAS spectra in the altitude range from 40 to 100 km are very sensitive to the collisional rates  $k_{vv,2}$ ,  $k_{vv,3}$ ,  $k_{vv,4}$ ,  $k_{F1}$ ,  $k_{F2}$ , and  $k_{vt}$  (see Table 5.1). Furthermore, the different spectral responses and vertical structures of the perturbations of the rates provide independent information on each of the collisional parameters, and hence allows their joint retrieval and to gain information on their temperature dependencies. In the next section we further verify these results by applying the retrieval scheme to synthetic spectra.

## 5.5. Retrievals from synthetic spectra and error estimations

In this section we present the results of the joint inversion of the collisional rate coefficients and CO<sub>2</sub> vmr from synthetic spectra. The aim is to verify that the inversion scheme works as expected, to quantify how much information can be gained on each of the collisional rates, and to use this method to evaluate some systematic errors.

Synthetic spectra according to the MIPAS spectral specifications, including artificial NESR of 3 nW/(cm<sup>2</sup> sr cm<sup>-1</sup>), have been computed for the mid-latitude, April 45°N reference atmosphere, SZA=44.5° (Funke et al., 2012) using the non-LTE populations shown in Figs. 5.8 and 5.9. Examples are shown in the top panels of Figures 5.10 and 5.11. We have performed retrievals of the state vector composed of the collisional rates  $k_{vv,2}$ ,  $k_{vv,3}$ ,  $k_{vv,4}$ ,  $k_{F1}$ ,  $k_{F2}$ , and  $k_{vt}$ , as well as the CO<sub>2</sub> abundance. The microwindows used in the joint retrieval are shown in Fig. 5.5, and by the grey shaded regions in Figs. 5.10 and 5.11, for the 4.3 μm region. Note that they change with the tangent height and they cover emissions from all the 4.3 μm bands sensitive to these parameters (see Table A.1). Additional micro-windows in the 10 μm region in the lines arising from the 00011→10002 band have also been included (see Fig. 5.6).

In the inversion of MIPAS spectra we have also derived the temperature dependencies of these rates, i.e., we have retrieved  $\alpha$  in  $k = k_0 (300/T)^\alpha$ . This has been carried out in an iterative way by varying the parameter  $\alpha$  and minimizing the  $\chi^2$  of the residuals. In these simulations, however, we assumed that this dependence, i.e.,  $\alpha$ , was known.

The joint retrieval of the collisional rates and CO<sub>2</sub> was performed with initial guess rates equal to the true values perturbed by 20%. The CO<sub>2</sub> profile was systematically perturbed by a 5% increase at 60-90 km and by a 20% increase above 90 km.

The results showed that all inverted parameters were retrieved within  $\pm 1\%$  of their true values, and thus that the retrieval was not over-regularized by the applied constraint. The CO<sub>2</sub> profile was also retrieved simultaneously with maximum deviations from the true profile smaller than 1% below 95 km, 1% at 100 km and 3% at 110 km.

Given the moderate vertical resolution of the retrieved CO<sub>2</sub> vmr profile ( $\sim 4$  km), we have also estimated the impact of a possible systematic bias in the a priori CO<sub>2</sub> profile, particularly around the homopause, where CO<sub>2</sub> abruptly decreases with altitude (see Figure 5.13). This has been done by performing the retrieval with a different a priori CO<sub>2</sub> profile taken from SD-WACCM simulations for Prandtl numbers of  $P_r=4$  (instead of  $P_r=2$  used in the standard case). Garcia et al. (2014) have shown that the change in this parameter, equivalent to change the eddy diffusion parameter, significantly changes the altitude where CO<sub>2</sub> starts declining. The impact on the retrieved rates is negligibly small with deviations from the true values smaller than 0.1%. Hence, these results demonstrate the ability of the retrieval scheme to simultaneously retrieve those rates and the CO<sub>2</sub> profile with a high precision and a reasonably weak dependence on the a priori assumptions.



We have used this method to perform sensitivity studies in order estimate some of the known parameter errors in the retrieval of these parameters. Among those, we know that the abundances of atomic oxygen,  $O(^3P)$ , and  $O(^1D)$ , not measured simultaneously with MIPAS spectra, significantly affect to the population of the  $CO_2$  levels (López-Puertas and Taylor, 2001; Kaufmann et al., 2002). The emission at  $4.3 \mu\text{m}$  also depends very much on the solar flux, mainly at  $4.3$  and  $2.7 \mu\text{m}$ .

$O(^3P)$  and  $O(^1D)$  abundances, below about 95 km, are photochemically constrained by the retrieved  $O_3$  from the same MIPAS spectra. Above 95 km, however, simultaneous  $O_3$  observations are not available.  $O(^3P)$  has a large variability and it is not well known in the mesosphere and lower thermosphere (Kaufmann et al., 2014). Following previous studies (García-Comas et al., 2012; García-Comas et al., 2014) we have considered a 50% uncertainty in the  $O(^3P)$  concentration.  $O(^1D)$  has different major sources in the stratosphere/lower mesosphere and in the upper mesosphere/lower thermosphere. In the lower region it is mainly produced by  $O_3$  photodissociation in the Hartley band (200-310 nm) (Brasseur and Solomon, 2005). Since the uncertainty in the solar flux in this spectral region is not very large, the  $O(^1D)$  uncertainty is dominated by the  $O_3$  retrieval accuracy, estimated to be within 10% below 80 km. In the upper mesosphere/lower thermosphere  $O(^1D)$  is mainly produced from the photodissociation of  $O_2$  in the Lyman- $\alpha$  and Schumann-Runge bands and continuum. The solar radiance at these wavelengths is rather uncertain (Ermolli et al., 2013) and the computation of the photo-absorption coefficient requires high spectral resolution. Overall we have considered an uncertainty of 30% in the abundance of  $O(^1D)$  above 80 km.

Solar fluxes near  $4.3$ ,  $2.7$ , and  $2.0 \mu\text{m}$  are calculated in the GRANADA model considering the time-dependent Sun-Earth distance. Attenuation by solar Fraunhofer lines is taken into account (Hase et al., 2006). The solar background radiance is expressed as a blackbody with an effective temperature  $T_e = 5450 + 0.25 \cdot (\tilde{\nu} - 2000)$ , being  $\tilde{\nu}$  wavenumber in  $\text{cm}^{-1}$ . This parametrization is similar to that developed by Platnick and Fontenla (2008) for  $3.7 \mu\text{m}$ , and they agree within 0.5-1% at that wavelength. On the other hand, the calculated solar flux agrees within 0.1% with that of Kurucz (1995) in the  $4.3$ ,  $2.7$ , and  $2.0 \mu\text{m}$  spectral regions. Based on these results we have assumed an error of 1% in the solar fluxes. The mapping of these errors on the retrieved collisional rates is listed in Table 5.2. This table also includes other sources of errors as the gain calibration uncertainty of MIPAS, and the systematic error of temperature. The first was estimated to be in 1% in band D (Kaufmann et al. (2006), <http://www.atm.ox.ac.uk/group/mipas/err/>). However, more recent estimates suggest that this error is slightly larger, i.e., 1.25% [G. Perron, priv. comm.]. The temperature errors were taken as 1 K from 50 to 70 km, 2 K between 70 and 80 km and 5 K above (García-Comas et al., 2014).

We also included the error introduced by the uncertainty in the elevation pointing (tangent altitude). This is retrieved jointly with temperature from the  $15 \mu\text{m}$  spectral region (García-Comas et al., 2014). However, there is little information on it above  $\sim 60$  km. von Clarmann et al. (2003) estimated the total systematic error in the retrieved absolute pointing from  $15 \mu\text{m}$  to be less than 200 m. Kiefer et al. (2007)

Table 5.2: Errors of the rate coefficients retrieved in this work (see Table 5.1).

Rate	Errors (%)							Total
	Random	Gain (1.25%)	Temp. <sup>†</sup>	Tangent altitude	[O( <sup>3</sup> P)] (50%)	[O( <sup>1</sup> D)] <sup>‡</sup>	Solar flux(1%)	
$k_{vv2}$	0.16	4.0	0.6	0.81	0.05	1.4	2.6	5.1
$k_{vv3}$	0.09	1.9	3.5	0.30	0.06	0.8	0.18	4.1
$k_{vv4}$	0.08	1.8	0.6	0.08	0.38	0.07	2.7	3.3
$k_{F1}$	0.09	0.8	4.6	1.2	0.22	0.11	0.33	4.8
$k_{F2}$	0.09	1.5	3.1	2.2	0.11	0.23	0.61	4.1
$f_{vt}$	0.19	9.2	2.9	0.47	3.1	11	4.3	15

<sup>†</sup>1 K at 50-70 km, 2 K at 70-80 km; 5 K above 80 km. <sup>‡</sup>10% below 80 km and 30% above.

characterized the accuracy of the engineering information of the MIPAS elevation pointing and found that the relative pointing errors, i.e. uncertainties in the altitude differences between adjacent tangent altitudes, are on average about 200 m. Hence, in order to estimate the total systematic pointing error, both components (absolute and relative) have to be taken into account. Combining them quadratically leads to an uncertainty of 283 m, that constitute the pointing error included in the retrieved rates (see Table 5.2). Given the high spectral resolution of MIPAS, propagated errors arising from interfering species in this spectral region are negligible.

Table 5.2 shows that the major uncertainties in the  $k_{vv,2}$  rate originate from the gain and solar flux uncertainties, with a non-negligible contribution from O(<sup>1</sup>D). Adding all the sources quadratically they amount to a total error of 5.1%. The rate  $k_{vv,4}$ , affecting also solar-pumped levels, has similar error sources but the uncertainties induced by the gain and O(<sup>1</sup>D) are smaller. The uncertainty of the  $k_{vv,3}$  rate coefficient, affecting to the deactivation of levels not directly excited by solar radiation, is mainly driven by the temperature error. The same occurs to the  $k_{F1}$  and  $k_{F2}$  rate coefficients with overall errors of 4.8% and 4.1%, respectively. The error in the vibrational-thermal  $k_{vt}$  rate is, however, larger. Several sources contribute significantly: the gain, the kinetic temperature, atomic oxygen, the solar flux and, principally, the uncertainty in the concentration of O(<sup>1</sup>D).

## 5.6. Results

The results of the retrieved collisional rates for all of the daytime scans of the four days of MIPAS UA measurements are shown in Figure 5.12 as a function of latitude. The mean values are listed in Table 5.1. As discussed above we have retrieved the rates as well as its temperature dependence in the form of  $k = k_0 (300/T)^\alpha$  through an iterative process. The mesospheric temperature changes significantly with latitude and season. However, Figure 5.12 shows that the retrieved  $k_0$  values are essentially independent of latitude. This demonstrates that the retrieved temperature dependence, in the range of mesospheric temperatures, is very accurate. We estimated the error of  $\alpha$  following the same procedure as we did for its derivation. We found that a perturbation of 10% introduces an appreciable increase in the  $\chi^2$ ; so this can be

considered as an upper limit of its error.

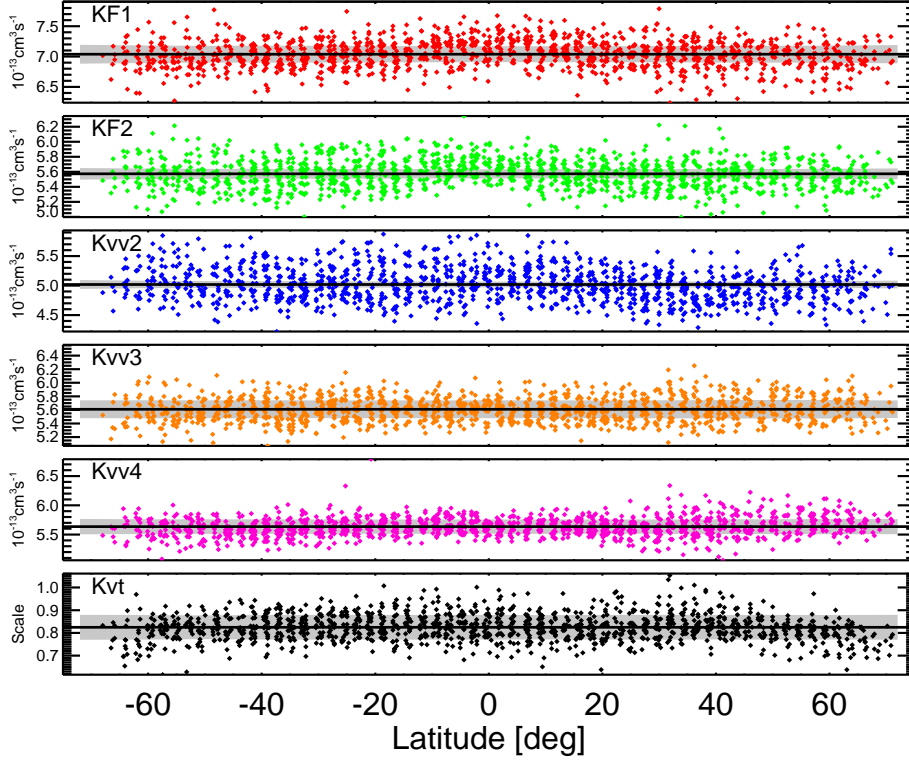


Figure 5.12: Retrieved collisional rates at 300 K,  $k_0$ , as function of scan latitude for all of the daytime scans of MIPAS spectra taken in the UA mode during 17 January, 30 March, 8 June and 26 September of 2010. The mean value from all latitudes is represented by solid lines. The grey shaded areas represent the noise error in the individual retrieved rates.

In Table 5.1 we also list the factor retrieved for the rate  $k_{O(^1D)}$ . This process enhances the population of  $N_2(1)$  and because of its strong  $k_{vv,0}$  coupling with  $CO_2$  also largely controls the population of 00011 in the mesosphere. This process has, however, the opposite effect of the thermal relaxation of 00011 by air molecules,  $k_{vt}$  (process 8 in Table 5.1), and hence could not be jointly retrieved with  $k_{vt}$  in the inversion. We then followed a similar strategy as for determining the rate temperature dependence. That is, we retrieve  $k_{vt}$  assuming different values for  $k_{O(^1D)}$ . The retrievals showed that for changes  $<50\%$  around the a priori values of the rates, we obtained a near one-to-one response. We then assumed as the best retrieved ( $k_{vt}$ ,  $k_{O(^1D)}$ ) pair the one that minimizes the  $\chi^2$  of the retrieval.

The retrieval noise, i.e. the mapping of the MIPAS NESR of  $3 \text{ nW}/(\text{cm}^2 \text{ sr cm}^{-1})$  into the rates, is generally very small (see grey shaded areas in Figure 5.12). However, the dispersion of the retrieved values is much larger than the noise error for all the rates. This suggests that the dispersion is caused by the random variability (stochastic errors) of the atmospheric parameters. Hence we have estimated the random error of the retrieved collisional rates (see Table 5.2), including the propagated uncertainties of not accurately known parameters, as the standard error of the retrieved values derived

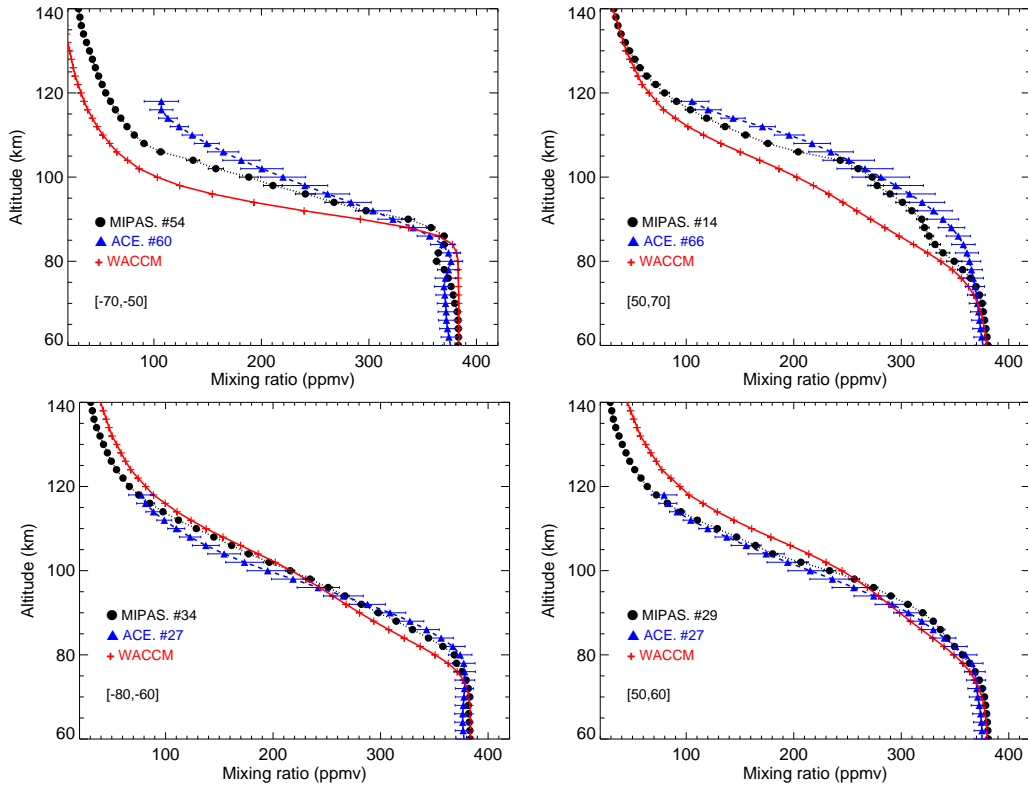


Figure 5.13:  $\text{CO}_2$  vmrs retrieved jointly with the collisional rates and compared with co-located ACE measurements and the *a priori* SD-WACCM ( $P_r=2$ )  $\text{CO}_2$  profiles. Top: solstice conditions (17 Jan 2010) for southern (polar summer) and northern (polar winter) conditions (left and right panels, respectively); and bottom: equinox conditions (30 March 2010) (left and right, respectively). The error bars in the ACE profiles are the total (random and systematic errors) (Beagley et al., 2010; Garcia et al., 2014). The small error bars of MIPAS represent only the noise error.

from all scans (see Figure 5.12).

As mentioned above, we have retrieved the  $\text{CO}_2$  vmr jointly with the collisional rates. Although we have found (see Section 5.5) that there is only little dependence of the retrieved collisional rates on the  $\text{CO}_2$  *a priori* profile, one may ask if the retrieved  $\text{CO}_2$  is plausible, or if it is unrealistically biased. The latter could hint at a not yet identified systematic error source. Figure 5.13 shows the retrieved  $\text{CO}_2$  profiles compared with co-located ACE measurements. There are very few contemporary measurements of  $\text{CO}_2$  in the middle and upper atmosphere, only from ACE (Beagley et al., 2010) and SABER (Mertens et al., 2009; Rezac et al., 2015; Yue et al., 2015). SABER uses also the limb emission technique while ACE, using the solar occultation approach, is not affected by non-LTE. Hence ACE observations were taken here for comparison. The  $\text{CO}_2$  from SD-WACCM simulations ( $P_r=2$ ), which is used as *a priori* in the retrieval, is also shown for comparison. Due to the absorption technique used by ACE, there are very few profiles available for comparison (and located essentially only

at two different latitudes). In order to get a meaningful statistic we then considered the ACE measurements taken with  $\pm 3$  days of the MIPAS measurements. We see that overall there is a very good agreement between the  $\text{CO}_2$  of ACE and MIPAS. During solstice conditions (upper panels), the agreement is not as good but still within the error bars below  $\sim 100$  km. Only during polar summer at altitudes above  $\sim 100$  km, ACE and MIPAS profiles diverge, with MIPAS lying between the profile predicted by SD-WACCM and that measured by ACE. At northern latitudes the agreement is better. For equinox conditions, when the temperature and  $\text{CO}_2$  gradients in the upper mesosphere/lower thermosphere are generally less pronounced, the agreement between ACE and MIPAS is excellent. In conclusion, the comparison of the jointly retrieved  $\text{CO}_2$  vmr profiles to independent observations provides no hint at a systematic bias of the retrieved rates.

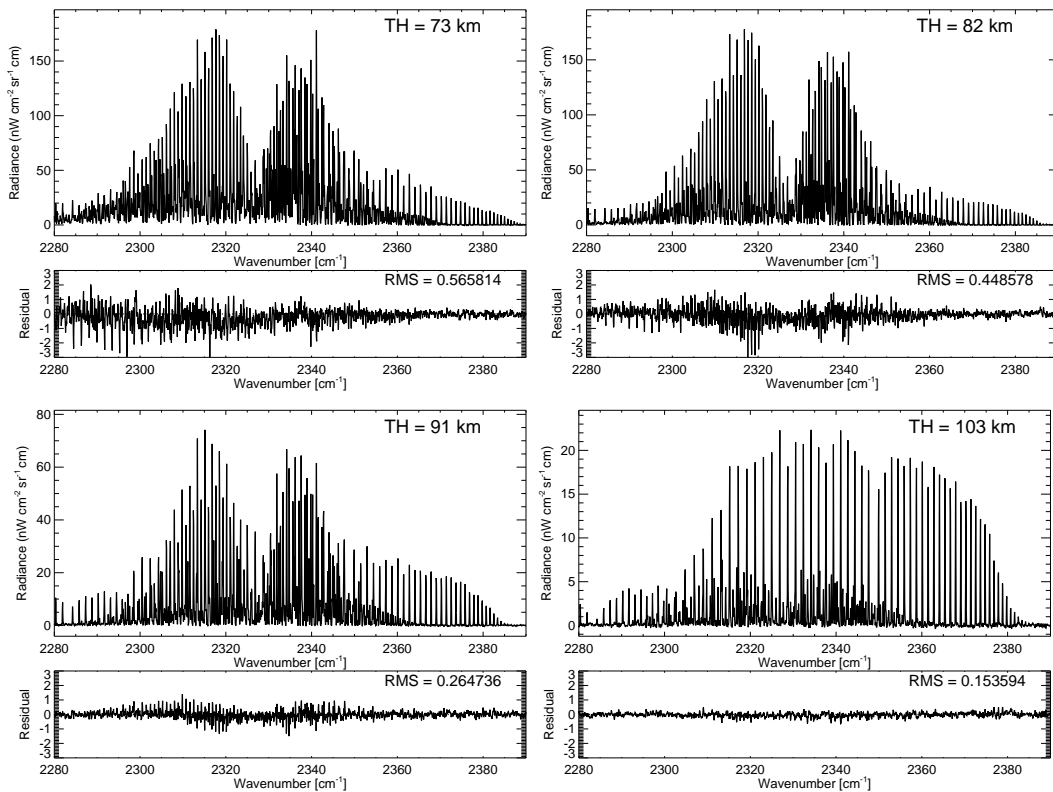


Figure 5.14: Co-added measured spectra (upper panels) and residuals, simulated–measured, (lower panels) at tangent heights of 73, 82, 91, and 103 km obtained from the retrievals for the four analysed days. The residuals are in the same radiance units of  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ .

For a further check of the quality of the retrievals we looked at the spectral residuals at several tangent heights (see Figure 5.14). The residuals still show some systematic differences at lower tangent heights (73 km), but they are very small, in the order of  $\pm 1\text{--}2 \text{ nW}/(\text{cm}^2 \text{sr cm}^{-1})$ , which is only  $\sim 1\%$  of the signal. At smaller wavenumbers ( $2280\text{--}2320 \text{ cm}^{-1}$ ), a large fraction of these differences can be attributed

to the 4.3  $\mu\text{m}$  fundamental band of second isotopologue, whose collisional rate with  $\text{N}_2(1)$  was not retrieved here. This suggests that it is slightly different from the value for the most abundant isotopologue. Since ro-vibrational lines of the second isotopologue's fundamental band have been excluded from the micro-window selection, no impact on the retrieved rates is expected.

At 82 km the signal is very similar to that at 73 km but the root mean square (RMS) has decreased by a factor of 1.3, leading to an even better simulation of the measurements. The major reason is the better simulation of the mentioned isotopic band. At 91 km, the residuals are smaller, even in relative terms. We still appreciate some systematic residuals coming mainly from the second hot bands. However, given the excellent agreement of the observed and modelled band-averaged radiances (see below), these residuals are most likely introduced by a systematic error in the kinetic temperature distorting the rotational distribution. At higher altitudes, we observe that the measured spectra are very well reproduced. Overall, we have not found any significant feature (i.e. larger than  $\simeq 1\text{-}2\%$  of the signal) in the residuals, which provides confidence on the retrieved collisional rates.

To show more clearly the residuals in the different  $\text{CO}_2$  4.3  $\mu\text{m}$  bands (see Table A.1), we calculated the band-averaged radiance contributions in the measured and simulated spectra (see Figure 5.15). These were computed by weighting the total spectra by the line intensities of the corresponding band and normalizing it. Hence, they do not strictly represent the band contributions, since overlap and non-linearity in the radiative transfer are not properly taken into account, but are a good estimate of their contributions. Thus, some bands with strong overlap, as FrH2 and FrH3 (see Table A.1), were not shown. The very good agreement between measurements and simulations in all the bands and at all tangent heights is remarkable. The deviations are generally within  $\pm 2\text{-}3\%$ , and only at the uppermost tangent heights (above 115 km), where the signal-to-noise is smaller, the percentage deviations are slightly larger.

## 5.7. Discussion

In this section we discuss the retrieved collisional rates in the light of the values used in previous works and their effects on the  $\text{CO}_2$  4.3  $\mu\text{m}$  atmospheric emission. The rate  $k_{vv,0}$  has not been retrieved here but it is discussed for completeness. This rate was measured by Inoue and Tsuchiya (1975) in the 150-300 K temperature range and it has been used as  $k_{vv,0} = 5 \cdot 10^{-13} \sqrt{300/T}$  (see Table 5.1 and Figure 5.16a) in practically all the studies of the  $\text{CO}_2$  atmospheric emission at 4.3  $\mu\text{m}$  carried out so far. Thus, it was used in the analysis of SAMS measurements (López-Puertas and Taylor, 1989), of SPIRE observations (Nebel et al., 1994), and also introduced in the model of Shved et al. (1998) that was used in the retrieval of  $\text{CO}_2$  from CRISTA spectra (Kaufmann et al., 2002) and more recently from SABER measurements (Rezac et al., 2015). By the way, we noted a typographical error in process 7 of Shved et al. (1998), where it should be  $1/\sqrt{T}$  instead of  $\sqrt{T}$ . The same rate was used by Funke et al. (2012). Only the analysis of ISAMS measurements (López-Puertas et al., 1998a,b) suggested that a factor between 0.8 and 1.0 times the rate of Inoue and Tsuchiya

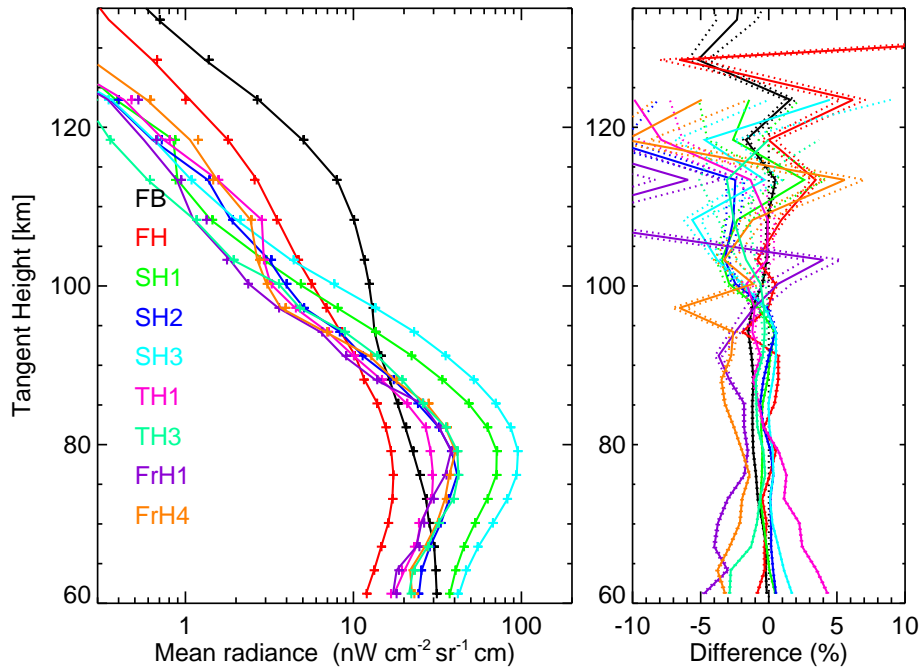


Figure 5.15: Measured (symbols) and simulated (lines) mean radiances in the 2280-2400  $\text{cm}^{-1}$  interval) of different  $\text{CO}_2$  4.3  $\mu\text{m}$  bands (left panel) (see Table A.1) obtained in the retrievals for the four analysed days (see Fig. 5.14). Right panel shows the differences (simulated-measured) in percentage and their standard deviations (dotted lines).

(1975) was consistent with ISAMS radiances taken at a SZA lower and higher than  $60^\circ$ , respectively. In our analysis we use the fit  $k_{vv,0} = 4.64 \cdot 10^{-13} (300/T)^{0.64}$  to the measurements of Inoue and Tsuchiya (1975), which is very similar to the usual form of  $k_{vv,0} = 5 \cdot 10^{-13} \sqrt{300/T}$  (see Figure 5.16a).

The rate coefficient  $k_{vv,1}$ , where the excited state of  $\text{CO}_2$  is 01111, has been taken equal to the rate  $k_{vv,0}$  of the V-V exchange between  $\text{CO}_2(00011)$  and  $\text{N}_2$  in all the studies mentioned above. Our simulations show that there is little sensitivity to this parameter (see Figure 5.8, 3rd row) and hence has not been retrieved here. We have also assumed the same value as for  $k_{vv,0}$ .

The rate coefficient  $k_{vv,2}$  is crucial for calculating the atmospheric radiation near 4.3  $\mu\text{m}$  at upper mesospheric and lower thermospheric limb paths since the emission from the populations of the 10011 and 10012 levels, generating the second hot bands, are largely controlled by this rate. As for  $k_{vv,1}$ , this rate has also been taken equal to that of the fundamental band,  $k_{vv,0}$ , in all previous studies, including the analysis of the SPIRE emission near 2.7  $\mu\text{m}$  (Sharma and Wintersteiner, 1985), except for SAMS and ISAMS. López-Puertas et al. (1998a,b) found, as for  $k_{vv,0}$ , that a value between 0.8 and 1.0 times that of Inoue and Tsuchiya (1975) fitted better SAMS and ISAMS measurements. Note that López-Puertas and Taylor (1989) derived a rate twice that value but a subsequent analysis showed a factor of 0.8–1 (López-Puertas et al., 1998a,b). The value derived here is significantly larger at temperatures smaller than 300 K, ranging from a factor of 1 to 1.5 from 300 K to 130 K, which



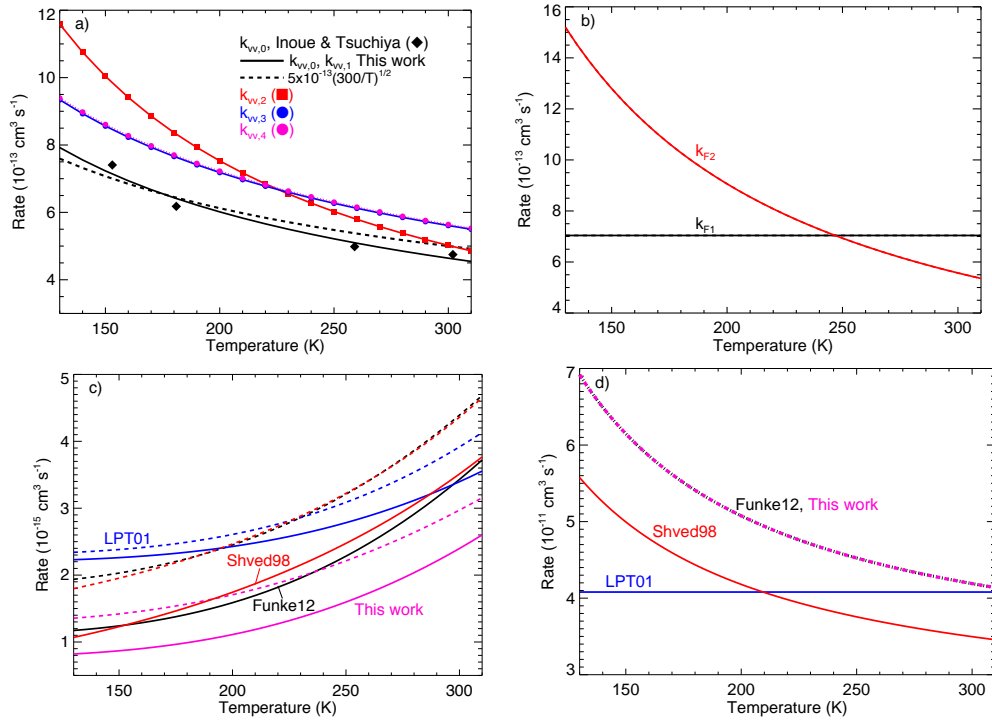


Figure 5.16: Temperature dependence of the collisional rates studied in this work. Panel a):  $k_{vv,0}$ - $k_{vv,4}$ . Panel b)  $k_{F1}$  and  $k_{F2}$ . Panel c)  $k_{vt}$ ; the solid lines represents collisions with N<sub>2</sub> and dashed lines collisions with O<sub>2</sub>. Panel d) excitation of N<sub>2</sub>(1) from O(<sup>1</sup>D). Labels indicate references as follows "Shved 98": Shved et al. (1998); "LPT01": López-Puertas and Taylor (2001); and "Funke12": Funke et al. (2012) (see text for more details).

is caused by the stronger temperature dependence retrieved here (compare red and black-dashed lines in Fig. 5.16a). This dependence could not be accounted for by the likely variability of, or change in, any other atmospheric or collisional parameter. This is a major result that significantly affects the 4.3  $\mu$ m atmospheric limb radiances at tangent heights below around 85-95 km, particularly at polar summer conditions.

The rates for the V-V collisional energy exchange between N<sub>2</sub> and the high-energy levels CO<sub>2</sub>( $v_d, v_3=1$ ) with  $v_d=2v_1+v_2=3$  and 4,  $k_{vv,3}$  and  $k_{vv,4}$ , have also been considered equal to  $k_{vv,0}$  in most of previous analysis. Only Funke et al. (2012) considered these rates to be different from  $k_{vv,0}$ , but they have not been used in the analysis of previous measurements. Here we have retrieved a temperature dependence slightly stronger than  $1/\sqrt{T}$ ,  $\alpha=0.6$ , and the values at mesospheric temperatures are also larger than previous rates in about 20%. We have not found any significant difference between  $k_{vv,3}$  and  $k_{vv,4}$ .

The rates  $k_{F1}$  and  $k_{F2}$  retrieved here are shown in Fig. 5.16b. These rates were very uncertain and a large range of values has been used in previous studies. Sharma and Wintersteiner (1985) derived values of  $3 \cdot 10^{-11}$  and  $1.5 \cdot 10^{-13}$  cm<sup>3</sup>s<sup>-1</sup> for  $k_{F1}$  and  $k_{F2}$ , respectively, from their analysis of the spectrally resolved SPIRE measurements



near  $2.7 \mu\text{m}$ . They distinguished between the rate for process  $\text{CO}_2(02211) + \text{M} \rightleftharpoons \text{CO}_2(10011)$  ( $k_{F2}$ ) and  $\text{CO}_2(10012) + \text{M} \rightleftharpoons \text{CO}_2(02211)$  ( $k_{F2'}$ ), the latter being a factor 2 larger than the former. They made a thorough analysis of the spectra and concluded that those figures could be considered as lower limits. SAMS and ISAMS measurements near  $4.3 \mu\text{m}$  are less sensitive to these rates. López-Puertas and Taylor (1989) and López-Puertas et al. (1998a,b) analysed those observations including values of  $2 \cdot 10^{-11}$  and  $2.4 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . These values were based on the measurements of Jacobs et al. (1975) of  $2 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  for the re-distribution between the 10001 and 10002 levels, and on the results of Finzi and Moore (1975) who found that the redistribution of the  $v_1$  and  $v_2$  quanta is independent of the vibrational excitation of the  $v_3$  mode. The  $k_{F1}$  and  $k_{F2}$  rates used in the model of Shved et al. (1998), which was used in the retrieval of  $\text{CO}_2$  from CRISTA (Kaufmann et al., 2002) and from SABER measurements (Rezac et al., 2015), are  $1.5 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  for  $k_{F1}$  and  $k_{F2}$ , and  $3.0 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  for  $k_{F2'}$ . Note that these rates differ significantly from those used in the other studies. We have retrieved a value of  $7.04 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  for  $k_{F1}$ , constant with temperature; and larger values for  $k_{F2}$ ,  $5.57 \times 10^{-13} (300/T)^{1.2} \text{ cm}^3 \text{ s}^{-1}$ , with a significant temperature dependence. The value for  $k_{F1}$  is about 43 times smaller than the rate derived by Sharma and Wintersteiner (1985), and about 4.7 times larger than that used by Shved et al. (1998). For  $k_{F2}$ , our rate is about a factor of 9 to 5 (4.5 to 2.5 for  $k_{F2'}$ ) larger than those used by Sharma and Wintersteiner (1985) and Shved et al. (1998) for temperatures of 150 and 250 K, respectively. However, it is a factor of 2 to 3.5 (4 to 7 for  $k_{F2'}$ ) smaller for the same temperature interval when compared to those used in the SAMS and ISAMS analysis (López-Puertas and Taylor, 1989; López-Puertas et al., 1998b). Hence, we should expect significant changes in the simulation of atmospheric radiation of the three  $4.3 \mu\text{m}$  second hot bands when using the new retrieved rates.

The  $k_{vt}$  collisional rates used in previous works and those retrieved here are shown in Fig. 5.16c. The values reviewed by López-Puertas and Taylor (2001) (label 'LPT01') were used in the analysis of the SPIRE, SAMS, CLAES and ISAMS measurements (Nebel et al., 1994; López-Puertas and Taylor, 1989; Edwards et al., 1996; López-Puertas et al., 1998a,b). Shved et al. (1998) used significantly smaller values, particularly at mid- and low temperatures. Funke et al. (2012) revised the rates compiled in the review of López-Puertas and Taylor (2001) to lower values, which are very similar to those of Shved et al. (1998). In this work we have retrieved values which are a factor of 0.7 smaller than those used by Funke et al. (2012).

The  $k_{O(1D)}$  collisional rates and efficiencies used in previous works and those retrieved here are shown in Fig. 5.16d. In the analysis of SPIRE (Nebel et al., 1994), CLAES (Edwards et al., 1996), and ISAMS data (López-Puertas et al., 1998a,b), the rate measured by Amimoto et al. (1979) of  $2.4 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  was used with an efficiency in the transfer of electronic to vibrational energy of 25% ('LPT01' in Fig. 5.16d). Shved et al. (1998) used in their model a similar rate, which is larger at temperatures below  $\sim 210 \text{ K}$  and smaller at larger temperatures (Fig. 5.16d). More recently, Funke et al. (2012) has adopted the rate revised by Ravishankara et al. (2002) of  $2.1 \cdot 10^{-11} \exp(115/T) \text{ cm}^3 \text{ s}^{-1}$  and assumed an efficiency of 20%. Here we have derived a value equals to that used by Funke et al. (2012) with an error of

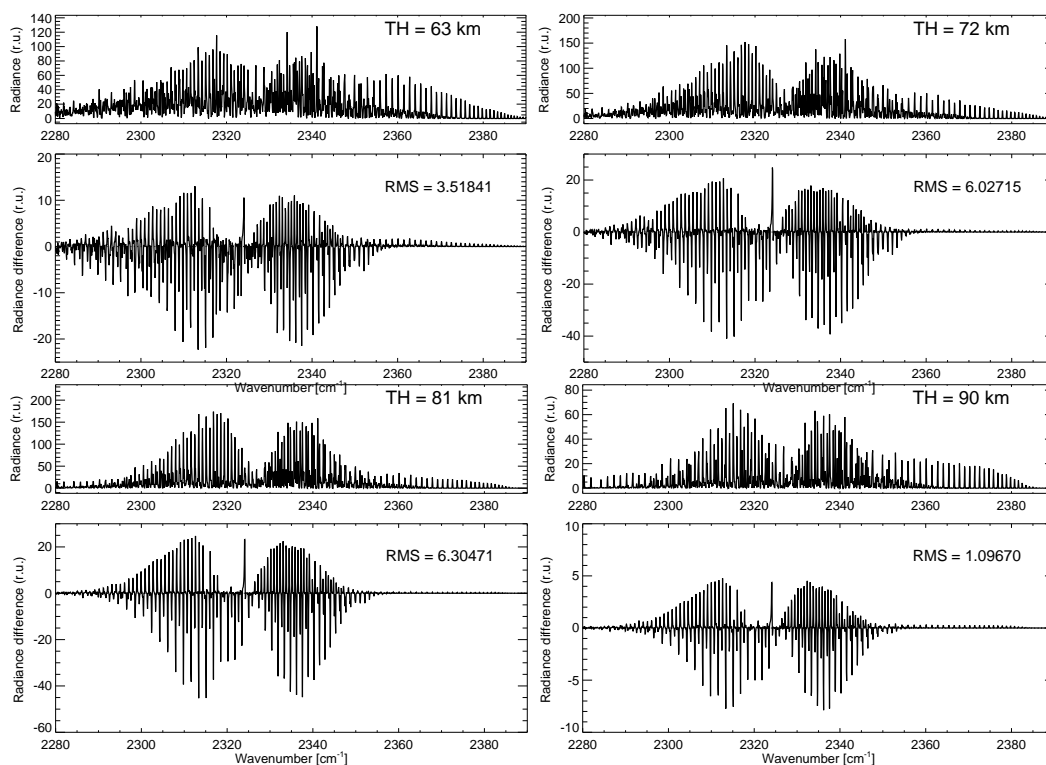


Figure 5.17: Simulation of MIPAS spectra for the retrieved rates and those mainly used in previous studies. Simulated spectra with the retrieved rates (upper panels) and differences (rates of this work—rates of previous works) (lower panels) at tangent heights of 63, 72, 81 and 90 km. Radiance units (r.u.) are in  $\text{nW}/(\text{cm}^2 \text{sr cm}^{-1})$ .

$\sim 15\%$ .

To show the impact of the retrieved rates on the atmospheric limb spectral radiance near  $4.3 \mu\text{m}$  we have performed simulations, for the April  $45^\circ\text{N}$  daytime ( $\text{SZA}=44.5^\circ$ ) and the polar summer January  $75^\circ\text{S}$  ( $\text{SZA}=58.7^\circ$ ) reference atmospheres, by utilizing a set of rate coefficients used in previous works and those retrieved here. As representative of previous works we have taken the rates of [Shved et al. \(1998\)](#). Compared to other previous studies, these authors use similar values for  $k_{vv,0}$ ,  $k_{vv,1}$ ,  $k_{vv,2}$ ,  $k_{vv,3}$  and  $k_{vv,4}$ , and intermediate values for  $k_{F1}$  and  $k_{F2}$ . Further, they use a  $k_{vt}$  rate very similar to the more recent rate used by [Funke et al. \(2012\)](#), and an intermediate rate for  $k_{O(1D)}$ . All atmospheric parameters were considered the same in these simulations. Fig. 5.17 shows the differences in the spectra at different tangent heights. Practically all bands are affected at these tangent heights showing very large differences in the spectral shape. Compare, for example, the RMS (root mean square) values obtained for these two simulations with those obtained in the retrieval. They are factors of 8, 13 and 4 larger for tangent heights of 72, 81 and 90 km, respectively.

The radiance in the emission of the second hot bands SH1 and SH3 is about 20-30% smaller for the retrieved rates for tangent heights below around 90 km. This is a consequence of the larger retrieved  $k_{vv,2}$  rate, leading to a significantly larger

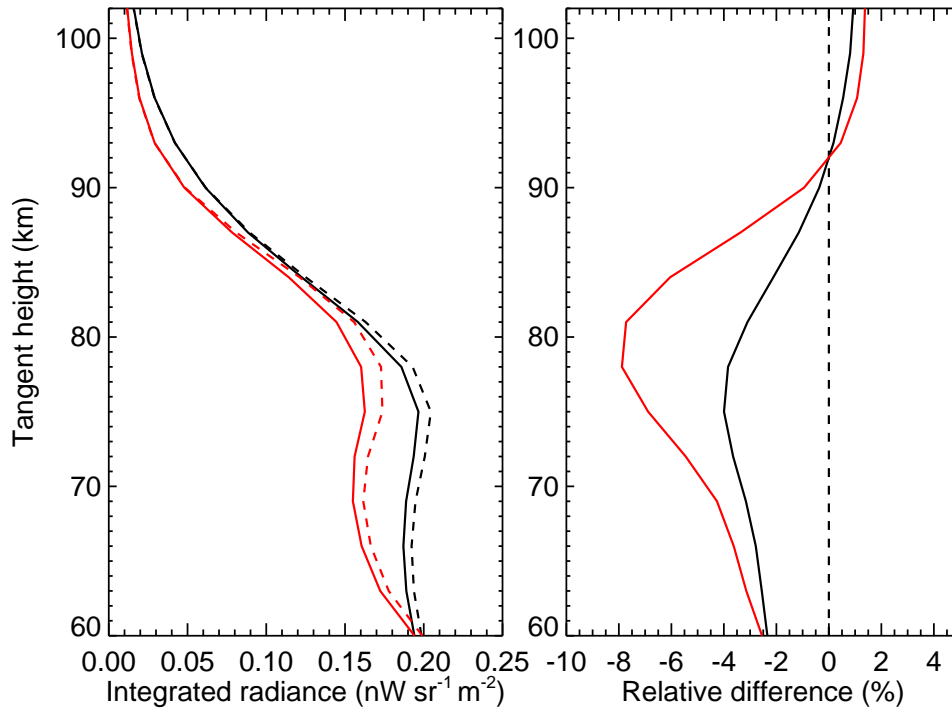


Figure 5.18: Effects of the new retrieved rates on atmospheric integrated radiance profiles. Left: Integrated limb radiance in the  $2280\text{--}2400\text{ cm}^{-1}$  spectral range calculated for the April  $45^\circ\text{N}$  ( $\text{SZA}=44.5^\circ$ ) (in black) and for the polar summer January  $75^\circ\text{S}$  ( $\text{SZA}=58.7^\circ$ ) (in red) reference atmospheres (Funke et al., 2012) for a case of collisional rates used in previous works (see text) (dashed) and those retrieved here (solid). The right panel shows the retrieved–previous work relative differences.

relaxation of the  $2.7\ \mu\text{m}$  levels. The emission of the SH2 band is, however, larger because of the larger retrieved  $k_{F2}$  rate, leading to a larger energy transfer from the states directly pumped by solar radiation (10011 and 10012) to 02211. As for the stronger SH1 and SH3 second hot bands, the emissions originating from the third and fourth hot bands are also smaller for the retrieved rates. This is also a consequence of the larger  $k_{vv,3}$  and  $k_{vv,4}$  rates retrieved here (compare  $k_{vv,3}$  and  $k_{vv,4}$  with the dashed line in Fig. 5.16a).

The population of the 00011 level, responsible for the  $4.3\ \mu\text{m}$  emission of the fundamental band as well as the  $10\ \mu\text{m}$  band laser emissions, is very important for the atmospheric studies. In the lower-middle mesosphere its population is controlled, besides the solar pumping in the  $4.3\ \mu\text{m}$  band, by the V-V excitation through  $\text{N}_2(1)$  from the  $2.7\ \mu\text{m}$  levels ( $k_{vv,2}$  followed by  $k_{vv,0}$ ), by the excitation of  $\text{N}_2(1)$  from  $\text{O}(^1D)$  ( $k_{O(^1D)}$ ), and by the V-T quenching with air molecules ( $k_{vt}$ ). The  $k_{vv,2}$  rate derived here is significantly larger than those used in previous works, the excitation from  $\text{O}(^1D)$  is similar, and the V-T thermal relaxation is moderately smaller. Overall, these processes lead to a larger excitation of 00011. In consequence the  $4.3\ \mu\text{m}$  fundamental band emission is larger for the new rates, in particular it is about 5% below around 90 km for mid-latitude conditions.

The overall effect for the integrated radiance in the 2280-2400  $\text{cm}^{-1}$  spectral range is shown in Fig. 5.18. The reduction in the second hot band dominates over the increase in the fundamental, resulting in a reduction in the radiance of 2-4% below about 85 km for mid-latitude conditions and as much as 8% in the polar summer. At the uppermost tangent heights, where the emission from the fundamental band dominates, there is a small increase in about 1%.

## Chapter 6

# CO<sub>2</sub> Retrieval from MIPAS Data

### *Abstract*

In this chapter, we present the major objective of this work: the inversion of CO<sub>2</sub> from MIPAS limb emission spectra. The retrieval setup is similar to that described in the previous chapter. The differences reside in the micro-windows used (selected from the 4.3  $\mu\text{m}$  solely), the temperature profiles above 95 km (taken from [Bermejo-Pantaleón et al. \(2011\)](#)), and the concentrations of O(<sup>1</sup>D), slightly changed to incorporate the solar cycle dependency. The values of the most important collisional rates affecting the populations of the CO<sub>2</sub> energy levels emitting in the 4.3  $\mu\text{m}$  spectral region are those derived in Chapter 5 (see also [Jurado-Navarro et al., 2015c](#)). The characterization of the retrieved CO<sub>2</sub> concentrations shows that the precision depends on altitude, varying from  $\sim 1\%$  below 90 km, to 5% around 120 km, and is larger than 10% above 130 km. The vertical resolution of the retrieved CO<sub>2</sub> is about 5–7 km below 120 km, with an increase of up to 12 km at  $\sim 100$  km, and between 10 and 20 km at 120–140 km. The analysis of the retrieved CO<sub>2</sub> from MIPAS is performed using the zonal monthly means (2010–2011), the annual mean (2010), and the inter-annual variability from 2010 to 2011. The retrieved MIPAS CO<sub>2</sub> has been compared to previous measurements taken by ACE and SABER, and with 3D global simulations of WACCM<sup>1</sup>.

### 6.1. Introduction

In this chapter we describe the inversion of CO<sub>2</sub> from MIPAS limb emission measurements in the 4.3  $\mu\text{m}$  spectral region. As mentioned in Chapter 2, MIPAS took measurements of the middle and upper atmospheres in three different measurements modes: MA, UA and NLC. Those of the UA mode, ranging from 42 to 172 km, were specifically devised for measuring the thermospheric temperature and NO abundance, and the abundance of CO<sub>2</sub>. In the other modes, MA and NLC, MIPAS took spectra up to 102 km but the emission of CO<sub>2</sub> above this tangent height is still very large and many CO<sub>2</sub> lines are still optically thick at those altitudes. Hence, because of this potential problem but also because we are able to retrieve CO<sub>2</sub> in a more extended altitude range we first focus on the retrieval of CO<sub>2</sub> from the UA mode. The problem turned out to be more complex than originally thought and henceforth this work is

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<sup>1</sup>A paper describing the results presented in this Chapter is currently in preparation.

focused on this atmospheric mode only, leaving for a future work the development of a retrieval baseline for the MA and UA modes.

MIPAS took measurements of the middle and upper atmosphere in those three modes from 2005 until April 2012. As explained below and in Chapter 5, the retrieval of CO<sub>2</sub> from MIPAS requires first the inversion of other parameters as the temperature (derived from the CO<sub>2</sub> 15  $\mu\text{m}$  emission) and O<sub>3</sub> below  $\sim 100$  km, and the thermospheric temperature (above  $\sim 100$  km) from the NO 5.3  $\mu\text{m}$  emission. At present, the thermospheric temperature (which is being retrieved simultaneously with the nitric oxide (NO) concentration, which, in turn, requires first the retrievals of other species in the inversion chain, e.g., NO in the mesosphere, NO<sub>2</sub>, CO and H<sub>2</sub>O) is only available for the measurements taken in 2010 and 2011. Therefore, at this time, we are limited to retrieving CO<sub>2</sub> from MIPAS spectra taken in the UA mode during 2010 and 2011. Nevertheless, since the measurements cover all seasons and latitudes this is not a significant limitation. Only the inter-annual variation in the 2005-2012 period could not be fully studied, although even some investigations could be performed (see Sec. 6.8).

## 6.2. Retrieval Setup

The retrieval of CO<sub>2</sub> is performed from MIPAS limb emission measurements of the 4.3  $\mu\text{m}$  spectral region. Besides the CO<sub>2</sub> vmr profile, another two parameters are fitted jointly in the retrieval: the line of sight (LOS), to correct pointing errors above 60 km, and the radiance offset to compensate offset calibration errors (Jurado-Navarro et al., 2015a,b). The scheme of the setup is similar to that described in detail in Jurado-Navarro et al. (2015c)<sup>2</sup>. The major differences regarding the CO<sub>2</sub> retrieval are: the altitude range, that embraces from 60 km to 142 km, and the selected micro-windows which are solely located in the 4.3  $\mu\text{m}$  spectral region, in MIPAS channel D (1820-2410  $\text{cm}^{-1}$ ).

The *a priori* information of CO<sub>2</sub> is taken from the SD-WACCM ( $P_r=2$ ) CO<sub>2</sub> climatology provided by Garcia et al. (2014) (see Chapter 5, Section 5.2). The CO<sub>2</sub> profile is regularized by means of a Tikhonov-type (Tikhonov, 1963) smoothing constraint. A strong diagonal constraint is added below 60 km in order to force the retrieved CO<sub>2</sub> to be close to the well-known mixing ratio in the lower mesosphere. Above 60 km, the constrain is optimized to obtain stable calculations with a high enough precision to allow for meaningful physical interpretation for the retrieved CO<sub>2</sub> abundance.

The temperature profiles used for the retrieval come from two sources: i) below 95 km, from the retrieval of temperature and LOS by García-Comas et al. (2014) (hereafter TLOS); and ii) above 95 km, from the joint retrieval of temperature and NO (nitric oxide) abundances by Bermejo-Pantaleón et al. (2011) (hereafter 'NOT'). The pressure profiles are implicitly derived from hydrostatic equilibrium. It is important to highlight that, in polar summer conditions, the temperature from NOT shows lower

<sup>2</sup>See also Chapter 5, Section 5.2

values than MSIS in the lower thermosphere of up to 10 K. Thus, the use of NOT temperatures instead of MSIS increases the retrieved CO<sub>2</sub> by up to 15% under these particular conditions.

Regarding the O(<sup>1</sup>D) profile, it has been improved compared to that used in the collisional rate retrieval in several aspects. First, the photoabsorption cross sections for O<sub>2</sub> have been updated including the experimental values of [Ogawa and Ogawa \(1975\)](#) and [Lu et al. \(2010\)](#). Secondly, the efficiency of O(<sup>1</sup>D) production from O<sub>2</sub> photo-absorption has been modified taking into account that below about 100 nm the O<sub>2</sub> ionization is the dominant channel. Thirdly, the effect of an overhead column proportional to the scale height of O<sub>2</sub> above the top layer of the model has been included. Furthermore, a variable solar spectral irradiance (SSI) input has been included in order to account for solar UV variations along the MIPAS observation period. SSI data has been taken from the NRLSSI model ([Lean et al., 2005](#)). This O(<sup>1</sup>D) photo-production has been compared with that calculated for similar conditions by an independent 1D model UV radiative transfer model ([González-Galindo et al., 2005](#); [Garcia et al., 2014](#)) finding differences smaller than 2% at all altitudes.

The used atomic oxygen, O(<sup>3</sup>P), profiles have been taken as for the retrieval of the collisional rates (see Chapter 5).

The CO<sub>2</sub> non-LTE model is based on that described in [Funke et al. \(2012\)](#) with the values of the main vibrational-vibrational and vibrational-translational processes retrieved from MIPAS spectra as described in Chapter 5 and summarized in Table 5.1 (see also [Jurado-Navarro et al., 2015c](#)).

### 6.3. Selection of the CO<sub>2</sub> Spectral Regions

The selection of the spectral regions sensitive to the CO<sub>2</sub> abundance is performed using the 4.3 μm Jacobians (see Figs. 5.1 and 5.2) and the selection method described in Chapter 5, Section 5.3. In this way, and thanks to the excellent MIPAS spectral resolution, we are able to select the spectral points sensitive to the CO<sub>2</sub> vmr while excluding lines with non-local responses due to spectral saturation. We have selected 18 principal microwindows within the 2300–2380 cm<sup>-1</sup> range, containing height-dependent sub-microwindows at 23 tangent heights from 60 km up to 142 km. In this altitude region, which embraces the lower mesosphere up to the lower thermosphere, we are able to obtain spectral points where the CO<sub>2</sub> non-LTE emission comes mainly from altitudes very close to the selected tangent heights and yet with a good signal-to-noise ratio.

An illustration of the selection based on the sensitivity of the spectral lines is shown in Figure 6.1. At 60 km, the fundamental band line (black) shows a local response and hence it is selected in the sub-micro-windows mask. On the contrary, the second hot lines (red and orange) do not give a local response (the maxima of the Jacobians are located at altitudes well above the tangent height) and hence are not selected. They are, however, included in the sub-microwindow mask for higher tangent heights, i.e. from 85 km up to 102 km, where they have quite enough local

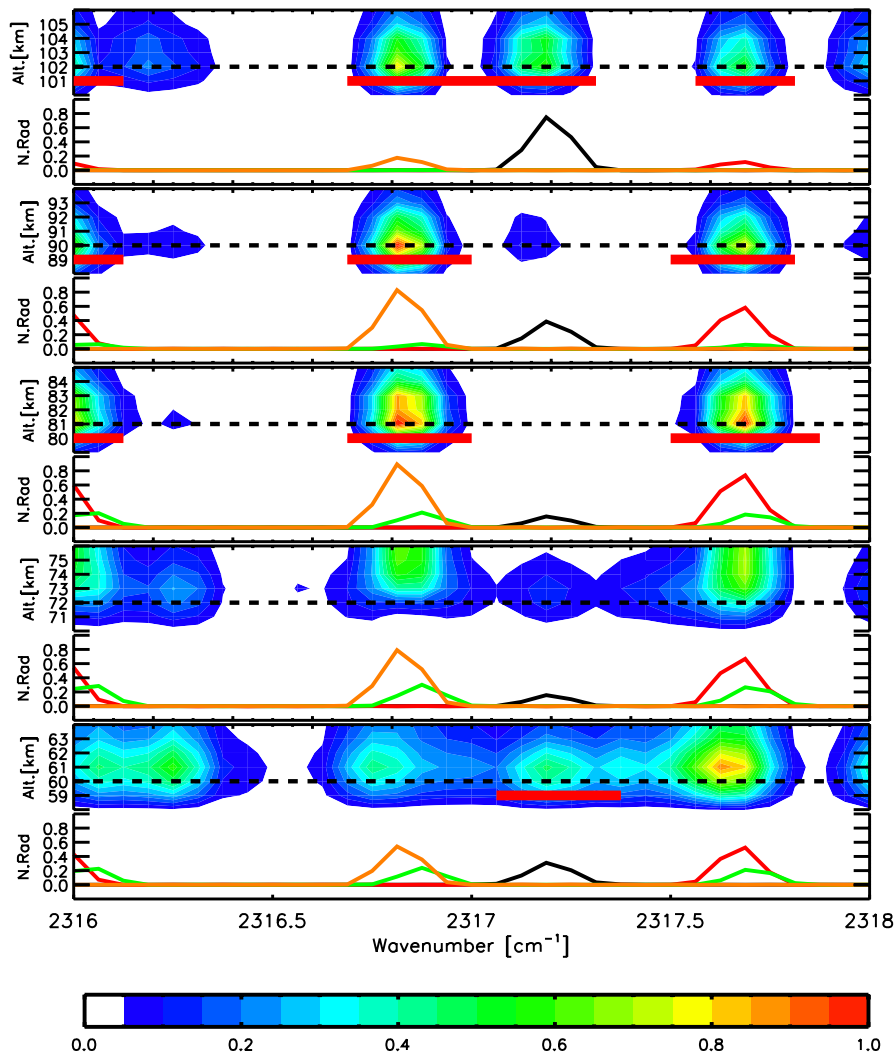


Figure 6.1: Jacobians and radiance for several lines in the 2316-2318  $\text{cm}^{-1}$  region for five different tangent altitudes (from bottom to top: 60, 72, 81, 90 and 102 km). Two panels are shown for each tangent altitude. Upper panel: normalized Jacobians at the corresponding tangent height; dashed black line stands for the tangent altitude and thick red line for the sub-microwindow mask. Lower panel: normalized radiance contributions for different lines of CO<sub>2</sub> bands; a line of the fundamental band in black, of the second hot  $10^0 1 \rightarrow 10^0 0$  band in red, of the  $02^2 1 \rightarrow 02^2 0$  band in green, and of  $02^0 1 \rightarrow 02^0 0$  in orange.

sensitivity. In this example the fundamental band line is not selected from 72 to 90 km, although it gives again valuable information at 102 km. Precisely, the 102 km altitude marks the transition height where the information from second hot band ends and that of the fundamental band starts.

In addition to the exclusion of spectral points with non-local response, we restricted the occupation matrix to the strongest lines at each altitude (mainly fundamental and second hot bands lines) for reasons of computational efficiency. Additionally, interferences from the 636, 628, 627, 638 and 637 CO<sub>2</sub> isotopologues have been



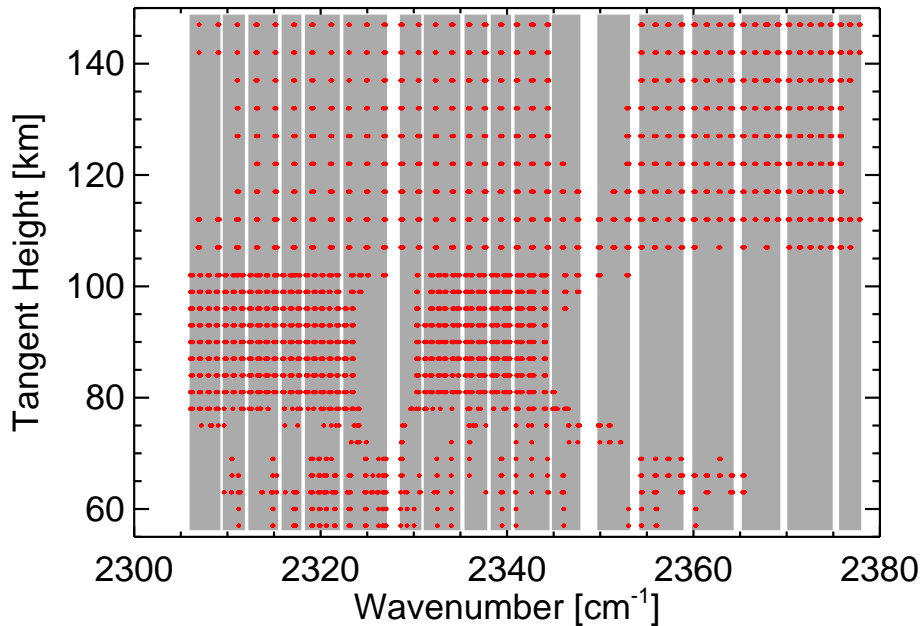


Figure 6.2: Occupation matrix used in the CO<sub>2</sub> retrieval in the 4.3  $\mu\text{m}$  spectral region. Shaded regions represent the microwindows selected and red dots the sub-microwindow mask at each tangent height.

suppressed in order to avoid systematic errors caused by the less accurate non-LTE modeling of these minor species.

An inspection of the resulting occupation matrix, shown in Fig.6.2, reveals that the selected spectral points belong mainly to the lines of the fundamental band in the 60-72 km and 102-142 km regions, and of the second hot bands in the 75-102 km region. More detailed information on the spectral lines contained in the sub-microwindows used in the retrieval of CO<sub>2</sub> is given in Table B.1.

## 6.4. Characterization of the Retrieved CO<sub>2</sub> vmr

### 6.4.1. Precision and Vertical Resolution

The vertical resolution and the precision are two important diagnostic parameters for characterizing the quality of any retrieval. Since the MIPAS measurements in the UA mode for 2010 and 2011 cover the four seasons twice, the zonal mean of these parameters are calculated for each season using 3 months: December-January-February, March-April-May, June-July-August and September-October-November (Figure 6.3).

In general, the precision varies with altitude ranging from  $\sim 1\%$  below 90 km, 5% around 120 km and larger than 10% above 130 km. The larger values at higher altitudes are due to the lower signal-to-noise ratio. There are very little latitudinal and seasonal variations, which are driven by the solar illumination conditions.

The vertical resolution is typically around 5–7 km below 120 km. Above that

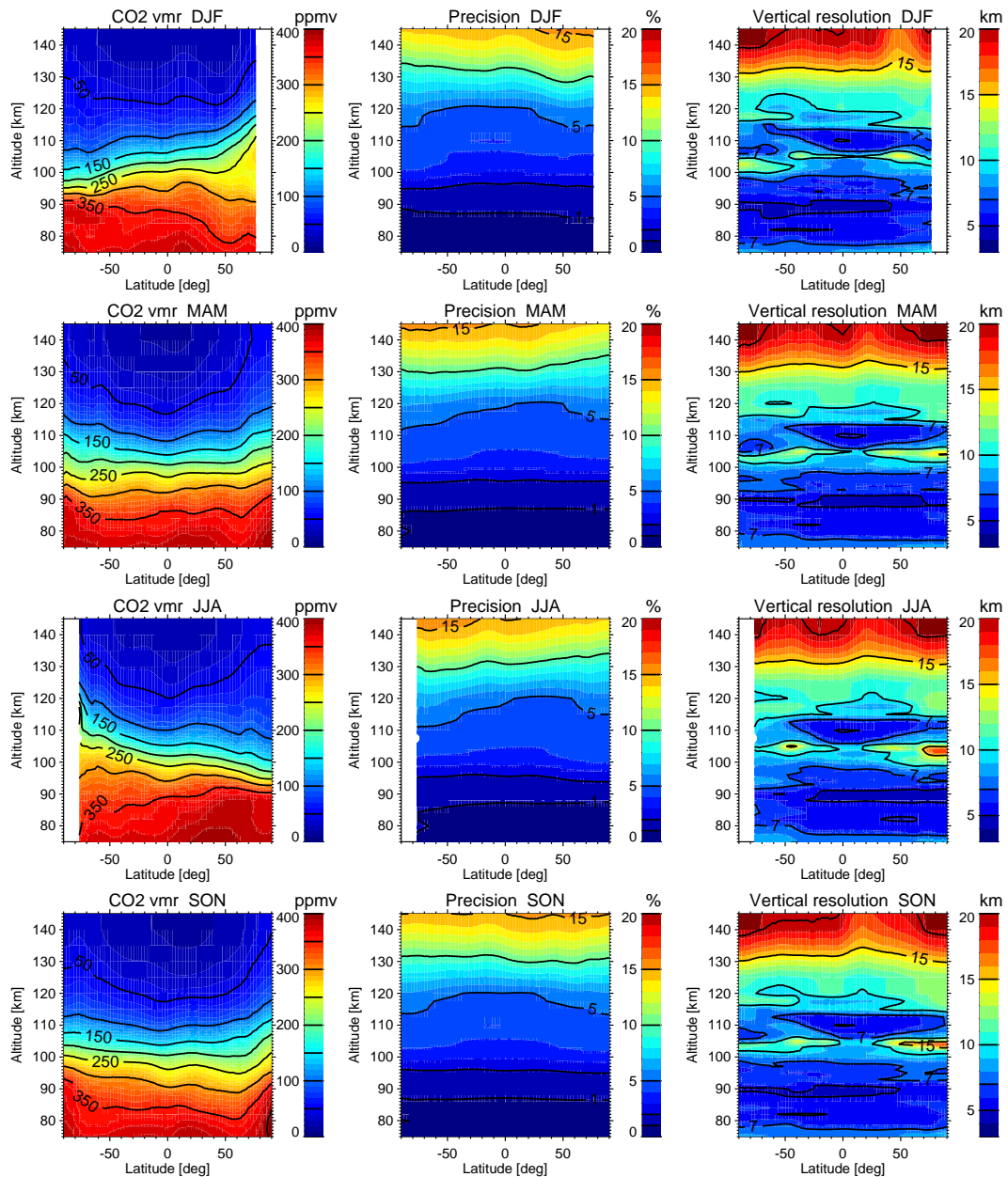


Figure 6.3: Latitude-altitude cross sections of CO<sub>2</sub> (left column), precision (centre column) and vertical resolution (right column). The rows, from top to bottom, correspond to the boreal winter (DJF: December-January-February), the vernal equinox (MAM: March-April-May), the austral winter (JJA: June-July-August) and the autumnal equinox (SON: September-October-November). The MIPAS data include the measurements taken in 2010 and 2011 in the UA mode.

altitude, it is poorer with values higher than 10 km. At  $\sim 102$  km, a sharp layer of increased vertical resolution (up to 12-13 km) is observed. This altitude corresponds to the tangent height where the sub-microwindows include lines from the second hot

bands only while the fundamental band lines are used above. The latter, as discussed above in Sec. 6.3, are still rather optically thick at this tangent height and hence have been rejected.

### 6.4.2. Retrievals from Synthetic Spectra

In order to test the performance of the retrieval setup, and following the same strategy than for the retrieval of the collisional rates (Chapter 5) [Jurado-Navarro et al.](#) (see also [2015c](#)), we have applied the retrieval setup of CO<sub>2</sub> to synthetic spectra calculated with KOPRA for a "known" atmosphere. This approach represents of course an idealized case in the sense that systematic retrieval errors are absent. Systematic errors are discussed in detail in the next section. We have performed synthetic retrievals for two different atmospheric conditions, one corresponding to mid-latitude equinox and the other to polar summer conditions. The major question to answer here is whether the retrieval yields reasonable results even in cases where the CO<sub>2</sub> and LOS *a priori* used is poorly representative for the actual atmospheric and instrumental conditions. Deviations of the retrieved profile from the "true" in these cases are often called smoothing errors. However, while it is important to assess the sensitivity of the retrieval to the *a priori* profile shape, we do not include smoothing errors in the overall error budget. First, because the concept of "smoothing errors" itself is questionable ([von Clarmann, 2014](#)), and secondly, because these deviations can be implicitly accounted for in comparisons to model simulations or independent observations by applying the MIPAS averaging kernels to the latter.

We investigate the sensitivity of the retrieval of CO<sub>2</sub> vmr to the CO<sub>2</sub> and LOS *a priori* profiles separately.

The CO<sub>2</sub> *a priori* profile was perturbed by exchanging the corresponding SD-WACCM profiles of the two atmospheric conditions, i.e. the mid-latitude SD-WACCM profile was implemented in the polar summer input and vice versa. Under mid-latitude conditions, the retrieved CO<sub>2</sub> profile differs from the true value by less than 2-3% in the whole altitude region (Figure 6.4 panels a and b). Compared to the difference with the *a priori* profile (up to 35%), the agreement of the retrieved profile and the "true" is excellent. Regarding polar summer conditions, the differences between the retrieved and the true profiles are generally smaller than 2% except at 95 to 110 km where it ranges at 2-4% (Figure 6.4 panels c and d). We have also tested the effect of the *a priori* when retrieving only the CO<sub>2</sub> vmr and keeping fixed the LOS (i.e., as a single-parameter retrieval). The result is shown by the green line in Fig. 6.4. We see that, for both atmospheric conditions, the differences between the retrieved CO<sub>2</sub> with and without the joint fit of LOS are only marginal. Also, the inspection of the retrieved LOS in the joint fit case (Fig. 6.5) shows that the mapping of the CO<sub>2</sub> *a priori* uncertainties on the LOS is very small (less than 20 m).

We also tested the impact of a perturbation of the LOS *a priori* information on the retrieved CO<sub>2</sub>. We applied a sine function perturbation to the LOS with a value of 0 m at 60 km and 142 km and a maximum of 200 m at 90 km. Above 90 km, the use of the perturbed *a priori* LOS profile in the CO<sub>2</sub>-LOS joint retrieval

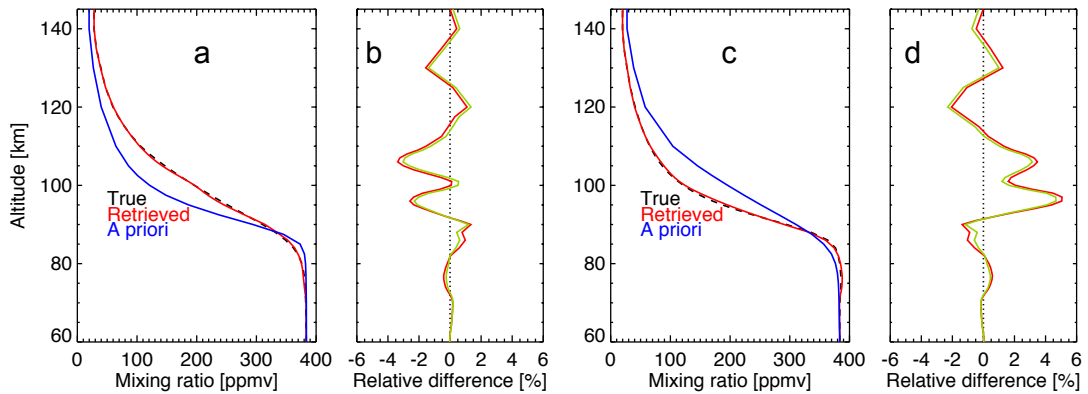


Figure 6.4: Sensitivity of the retrieved CO<sub>2</sub> profile to the a priori for mid-latitudes (panels a and b), and for polar summer conditions (panels c and d). The relative differences (panels b and d) are referred to the CO<sub>2</sub> and LOS joint retrieval (red solid line) and to the single-parameter CO<sub>2</sub> retrieval (green line).

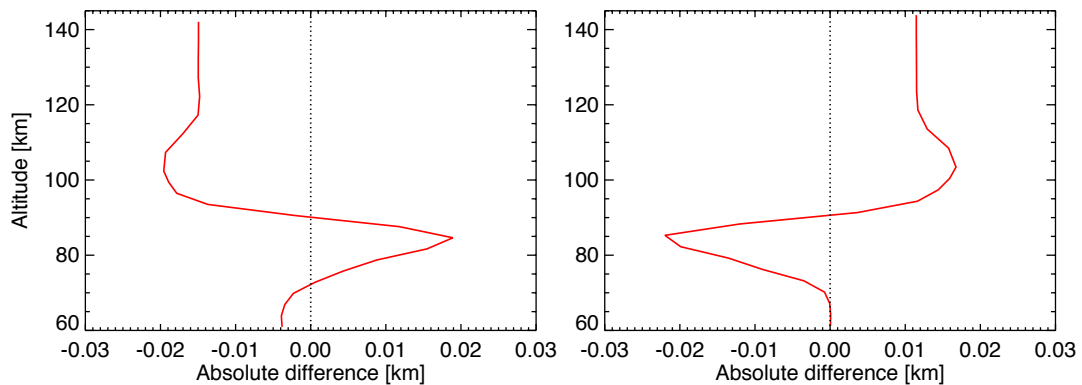


Figure 6.5: Sensitivity of the retrieved LOS to the CO<sub>2</sub> a priori uncertainties for mid-latitude (left) and polar summer (right) conditions. The lines show the retrieved-true LOS differences.

introduces deviations of the retrieved CO<sub>2</sub> from the true profile of less than 1–2%, while differences are negligible below (see Figure 6.6, red line). On the other hand, the application of the perturbed LOS in the single-parameter CO<sub>2</sub> retrieval introduces a significant systematic error of up to 3–4% for mid-latitudes and even larger (up to 5%) for polar summer in the whole altitude range above 70 km (see Figs. 6.6b and 6.6d, green lines).

Therefore, these results give us confidence on the retrieval scheme and we can conclude that the impact of *a priori* profile uncertainties on the retrieved CO<sub>2</sub> is very small,  $\lesssim 1\text{--}2\%$ . Furthermore, the inclusion of the LOS joint fit introduces no degradation on the retrieved CO<sub>2</sub> while it avoids important systematic errors due to LOS uncertainties.

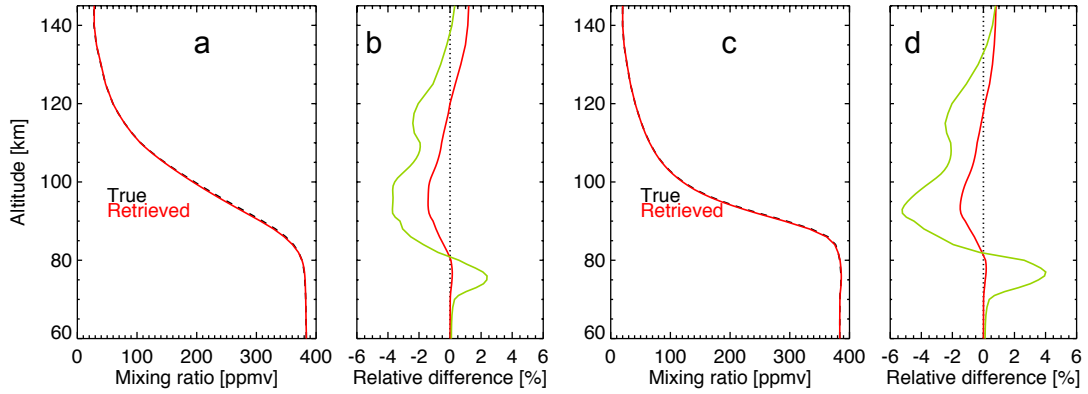


Figure 6.6: Sensitivity of the retrieved CO<sub>2</sub> to LOS a priori uncertainties for mid-latitude (panels a and b), and for polar summer conditions (panels c and d). The relative differences (retrieved–true) (panels b and d) are referred to the joint CO<sub>2</sub>-LOS retrieval (red solid line) and to the single-parameter CO<sub>2</sub> retrieval (green line).

### 6.4.3. Systematic Errors

The systematic errors were estimated from the retrieval response to perturbations of the following parameters: pressure/temperature, O(<sup>1</sup>D) and O(<sup>3</sup>P) abundances, MIPAS gain calibration and solar flux. The magnitudes of these perturbations are the same as those used in the retrieval of the collisional rates in Chapter 5 (see also [Jurado-Navarro et al., 2015c](#)), except for temperature that was assumed with an error of 5 K up to 100 km, 10 K between 100 and 110 km, and 15 K between 110 and 142 km. In addition, systematic CO<sub>2</sub> retrieval errors due to uncertainties in the collisional rates used in the non-LTE modeling need to be taken into account. However, since the CO<sub>2</sub> collisional parameters have been retrieved from MIPAS measurement in the same spectral region (see Chapter 5), using the same model parameters as used here in the CO<sub>2</sub> retrieval, the CO<sub>2</sub> retrieval errors due to systematic errors of the retrieved rates are expected to be correlated with the errors caused by model parameter uncertainties. Therefore, adding the systematic errors due to collisional rate uncertainties quadratically to the other errors would overestimate the total error. For instance, it might occur that an overestimation of the solar flux introduces a low bias of a certain collisional rate, but that the use of the hence underestimated rate in the CO<sub>2</sub> retrieval compensates the “direct” CO<sub>2</sub> error caused by assuming a too low solar flux. Therefore, we explicitly consider the propagation of errors due to pressure/temperature, O(<sup>1</sup>D), O(<sup>3</sup>P), gain calibration, and solar flux uncertainties of the collisional rate retrieval into the CO<sub>2</sub> retrieval by correcting the retrieval response  $\Delta CO_2^{i'}$  to perturbations of each model parameter  $i$  in the following way:

$$\Delta CO_2^{i'} = \Delta CO_2^i + \frac{\Delta K_{vv2,i}}{\Delta K_{vv2}} \Delta CO_2^{K_{vv2}} + \frac{\Delta K_{vv3,i}}{\Delta K_{vv3}} \Delta CO_2^{K_{vv3}} + \frac{\Delta K_{vv4,i}}{\Delta K_{vv4}} \Delta CO_2^{K_{vv4}} + \frac{\Delta K_{F1,i}}{\Delta K_{F1}} \Delta CO_2^{K_{F1}} + \frac{\Delta K_{F2,i}}{\Delta K_{F2}} \Delta CO_2^{K_{F2}} + \frac{\Delta f_{vt,i}}{\Delta f_{vt}} \Delta CO_2^{f_{vt}}, \quad (6.1)$$

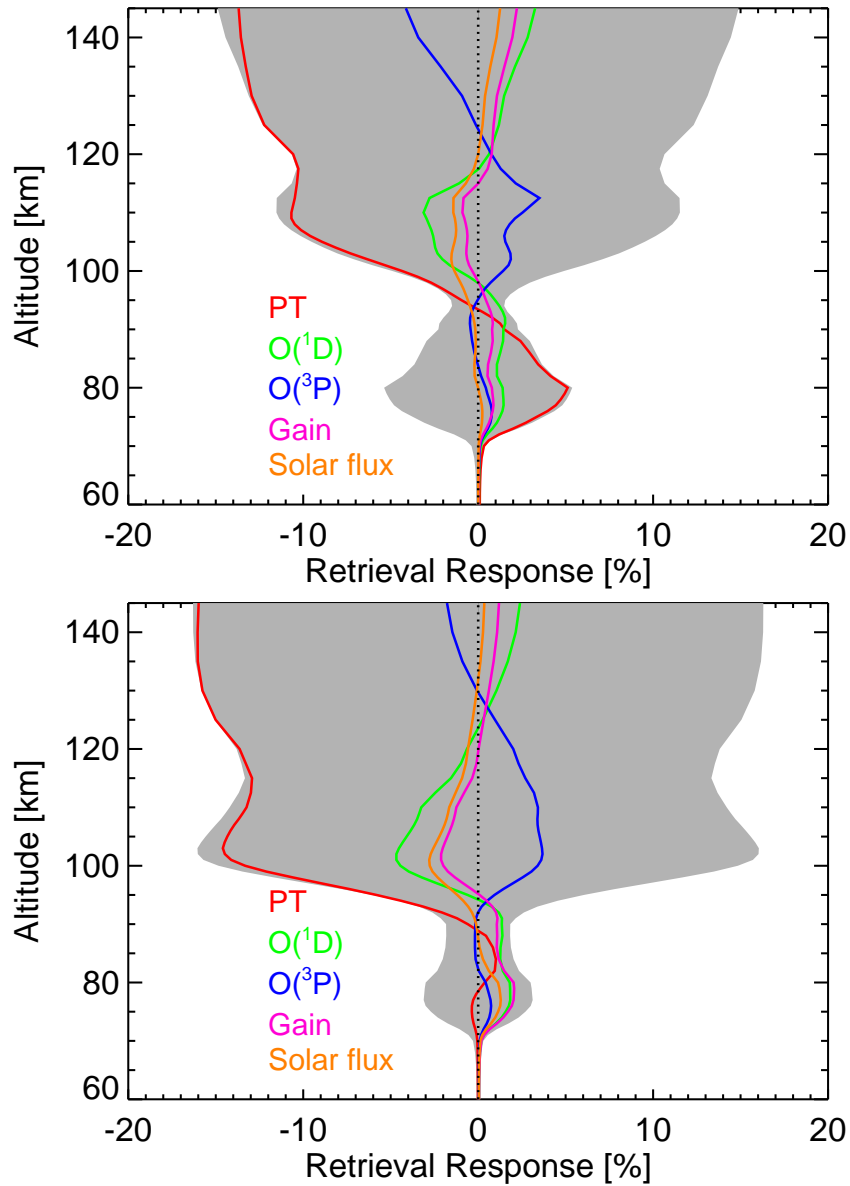


Figure 6.7: Systematic errors of the  $\text{CO}_2$  vmr introduced by different error sources for mid-latitude (top) and polar summer (bottom) conditions.  $\text{CO}_2$  retrieval responses to individual model parameter perturbations (reflecting their estimated uncertainties) are shown by the colored lines. The shaded area represents the total systematic error.

where  $\Delta CO_2^i$  is the “direct” response of the CO<sub>2</sub> retrieval to the model parameter perturbation.  $\Delta K_{vv2,i}$ ,  $\Delta K_{vv3,i}$ ,  $\Delta K_{vv4,i}$ ,  $\Delta K_{F1,i}$ ,  $\Delta K_{F2,i}$  and  $\Delta f_{vt,i}$  are the responses of the collisional parameter retrieval to the model parameter perturbation. These values have been taken the collisional rate error estimation described in Chapter 5 (Table 5.2).  $\Delta CO_2^{K_{vv2}}$ ,  $\Delta CO_2^{K_{vv3}}$ ,  $\Delta CO_2^{K_{vv4}}$ ,  $\Delta CO_2^{K_{F1}}$ ,  $\Delta CO_2^{K_{F2}}$  and  $\Delta CO_2^{K_{F2}}$  are the responses of the CO<sub>2</sub> retrieval to a perturbation of the respective collisional rate. The resulting corrected retrieval responses to the model parameter perturbations are shown in Fig. 6.7. The total systematic error is then calculated by quadratic summation:

$$\Delta CO_2^{TOTAL} = \sqrt{\sum_i (\Delta CO_2^{i'})^2}. \quad (6.2)$$

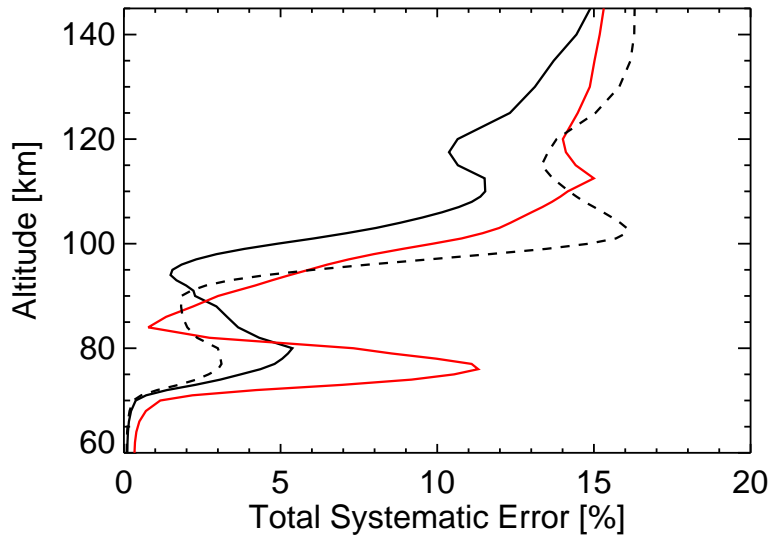


Figure 6.8: Total systematic errors of the main atmospheric parameters from the joint CO<sub>2</sub>-LOS (black solid line) and CO<sub>2</sub>-only (red line) retrievals for mid-latitude conditions. The dash black line shows the total systematic error of the joint CO<sub>2</sub>-LOS retrieval for polar summer. The total errors are calculated from the quadratic sum of the retrieval responses to individual model parameter perturbations shown in Fig. 6.8.

The calculations indicate that the largest error contribution above 100 km comes from the pressure/temperature uncertainties for both considered atmospheric conditions (Fig. 6.7), reaching values up to  $\sim 12\%$  in mid-latitude and  $\sim 16\%$  in polar summer conditions. Below, the pressure/temperature error maximizes again around 80 km, with maximum values at midlatitude conditions up to  $\sim 4\%$ . The MIPAS gain calibration and solar flux uncertainties introduce errors of 2-3% from 85 up to 110 km in both conditions. The total error below 90 km in polar summer conditions is indeed dominated by these uncertainties. The O(<sup>1</sup>D) and O(<sup>3</sup>P) uncertainties have a non-negligible contribution above 95 km with largest values up to 4% at 105 km in polar summer conditions.

Regarding the total systematic error, it is notably larger for the CO<sub>2</sub>-only retrieval

than for the joint CO<sub>2</sub>-LOS retrieval (see Fig. 6.8). This indicates that a large fraction of the spectral residuals due to systematic parameter errors is compensated by the LOS in the joint retrieval while in the single parameter CO<sub>2</sub> retrieval all errors map onto the CO<sub>2</sub> profile. In this sense, the joint CO<sub>2</sub>-LOS retrieval is also useful to dampen systematic errors of the retrieved CO<sub>2</sub>.

## 6.5. MIPAS CO<sub>2</sub> Climatology for 2010-2011

Figure 6.9 shows the monthly zonal mean CO<sub>2</sub> vmr measured by MIPAS in its UA mode. The figure shows the major features expected for the CO<sub>2</sub> distribution and predicted by models. Namely, the abrupt decline of the CO<sub>2</sub> vmr above around 80-90 km. The other major feature is the seasonal change of the latitudinal distribution, leading to higher CO<sub>2</sub> vmr from 70 up to ~95 km in the polar summer, induced by the ascending branch of the meridional circulation, and lower CO<sub>2</sub> abundances, with respect to the tropics and polar summer, at the same altitudes in the polar winter region. It is noticeable that the distribution reverses above ~95 km, CO<sub>2</sub> being more abundant in the polar winter region than at mid-altitudes and polar summer; also as a consequence of the reversal of the meridional circulation (see, e.g. Smith et al., 2011). The solstice seasonal distribution, with a significant pole-to-pole CO<sub>2</sub> gradient lasts for more than three months in each hemisphere (November through February, and May through August), while the seasonal transition occurs quickly, mainly in March and April, and September and October.

These figures show also another interesting feature. It appears that there is a region of low CO<sub>2</sub> near 80 km in polar summer (months of December and January near the South pole, and May-June-July near the North pole). This could be due to a remnant of CO<sub>2</sub>-poor air from the previous season, e.g., as it happens for CO, CH<sub>4</sub> and NO<sub>x</sub> but at low altitudes (Funke et al., 2014). However, we cannot discard the possibility that it could be due to a retrieval artifact caused by the complex and difficult situation of the very cold yet illuminated polar summer region.

Another observed feature is the rapid increase of CO<sub>2</sub> vmr from mid-high latitudes towards the polar regions in the lower thermosphere during equinoxes (more evident in April and October). We cannot find any physical reason for it and we do not discard that this could be a retrieval artifact caused by the inversion of CO<sub>2</sub> in conditions of very high (>80°) solar zenith angles.

## 6.6. Comparison of MIPAS CO<sub>2</sub> with ACE, SABER, and model data

Figures 6.10-6.13 show a comparison of MIPAS CO<sub>2</sub> abundances with those measured by the ACE and SABER instruments and SD-WACCM ( $P_r=2$ ) simulations for equinox conditions (March and September) and solstice conditions (June and December). Additional comparisons, for each month of the year, are shown



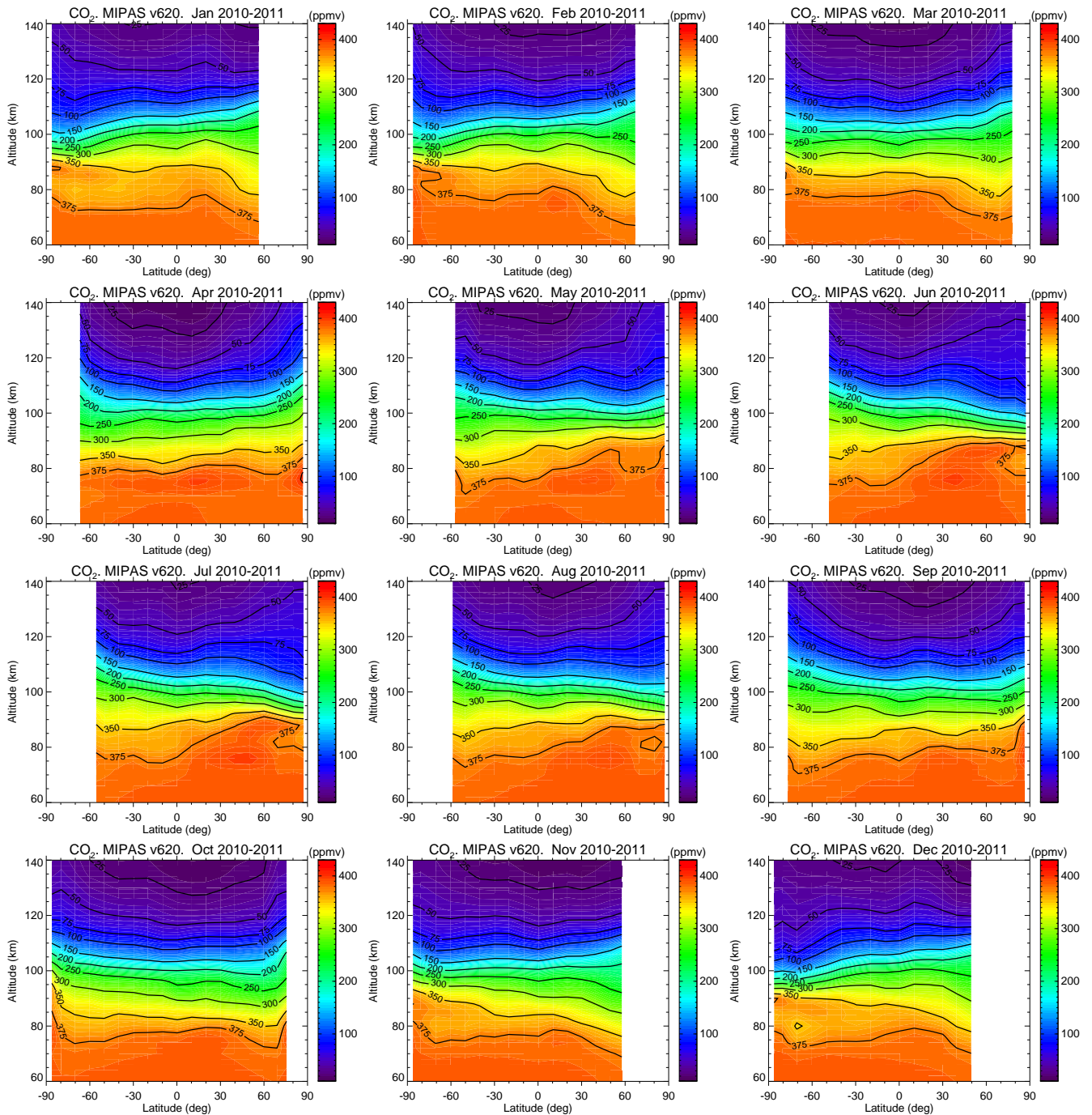


Figure 6.9: Monthly zonal mean CO<sub>2</sub> vmr measured by MIPAS during the 2010–2011 period for the UA mode.

in Appendix C), and will be referred to occasionally in the discussion that follows. Each figure shows the zonal mean distribution for each instrument and WACCM, the zonal mean differences of MIPAS with respect to ACE, SABER and WACCM, and two panels with CO<sub>2</sub> profiles for two latitudinal bands which correspond roughly to the ACE measurements during the given month. We use here version 3.5 of ACE <http://www.ace.uwa-terloo.ca/data.html> (Beagley et al., 2010; Emmert et al., 2012), which has been filtered by removing very physically unrealistic ('weird') profiles. For SABER we use the only version so far retrieved ([ftp://saber.gats-inc.com/Version2\\_0/Level2C/](ftp://saber.gats-inc.com/Version2_0/Level2C/)) (Rezac et al., 2015). As for WACCM, we use the model output for  $P_r=2$  as described by Garcia et al. (2014), which includes the most recent updates on the chemistry of CO and CO<sub>2</sub> in the middle and upper atmosphere. Also, the model version used here is the "Specified troposphere/stratosphere Dynamics" (SD) where WACCM is free running above 1 hPa and has been nudged to MERRA reanalysis below that pressure level. The horizontal bars in the panels that show vertical profiles corresponds to the total errors of the measurements, as reported in previous references for ACE and SABER and in Sec. 6.4.3 for MIPAS. In these figures they are dominated by the systematic errors.

We start the comparison for equinox conditions (Figs. 6.10 and 6.11). Starting with ACE, we observe an overall very good agreement. MIPAS CO<sub>2</sub> is slightly larger (~5%) between 80 and 100 km. At higher altitudes the differences vary with latitude, being comprised always within  $\pm 20\%$ . Excellent agreement is seen for March at 55°N-75°N. However, MIPAS CO<sub>2</sub> is significantly higher at 90–110 km in September at 75°S-55°S.

The agreement with SABER is even better, being within 5% below 100 km. Between 100 and 120 km, MIPAS tends to be larger (20–30%) in the polar regions, and smaller (~10-20%) near the Equator. It is noticeable that WACCM generally overestimates the CO<sub>2</sub> compared to the three instruments above ~90 km (except for September at 75°S-55°S) suggesting that a value for the Prandtl number of  $P_r=4$ , which would effectively reduce eddy diffusion by about a factor of two, would fit better the measurements (see also Sec. 6.7). This is also clearly shown in the bottom left panel of these figures. Another distinctive feature shown in WACCM results but not present in the measurements of any of the three instruments is the weaker decline of CO<sub>2</sub> above 95 km at mid-latitudes in the Southern and Northern Hemispheres (more prominent in March than in September). This might be due to a poor representation of the secondary meridional circulation associated with the semi-annual oscillation (SAO) in WACCM.

In solstice conditions (Figs. 6.12 and 6.13) the agreement among MIPAS, ACE and SABER measurements is also very good, despite of the stronger latitudinal gradient in CO<sub>2</sub> and the fact that the retrieval of CO<sub>2</sub> under stronger gradients of temperature and illumination conditions along the LOS is more challenging. The three instruments show the expected solstice zonal mean distribution –larger CO<sub>2</sub> in the polar summer and smaller in the polar winter–; its seasonal change, and the general patterns agree well with WACCM predictions.

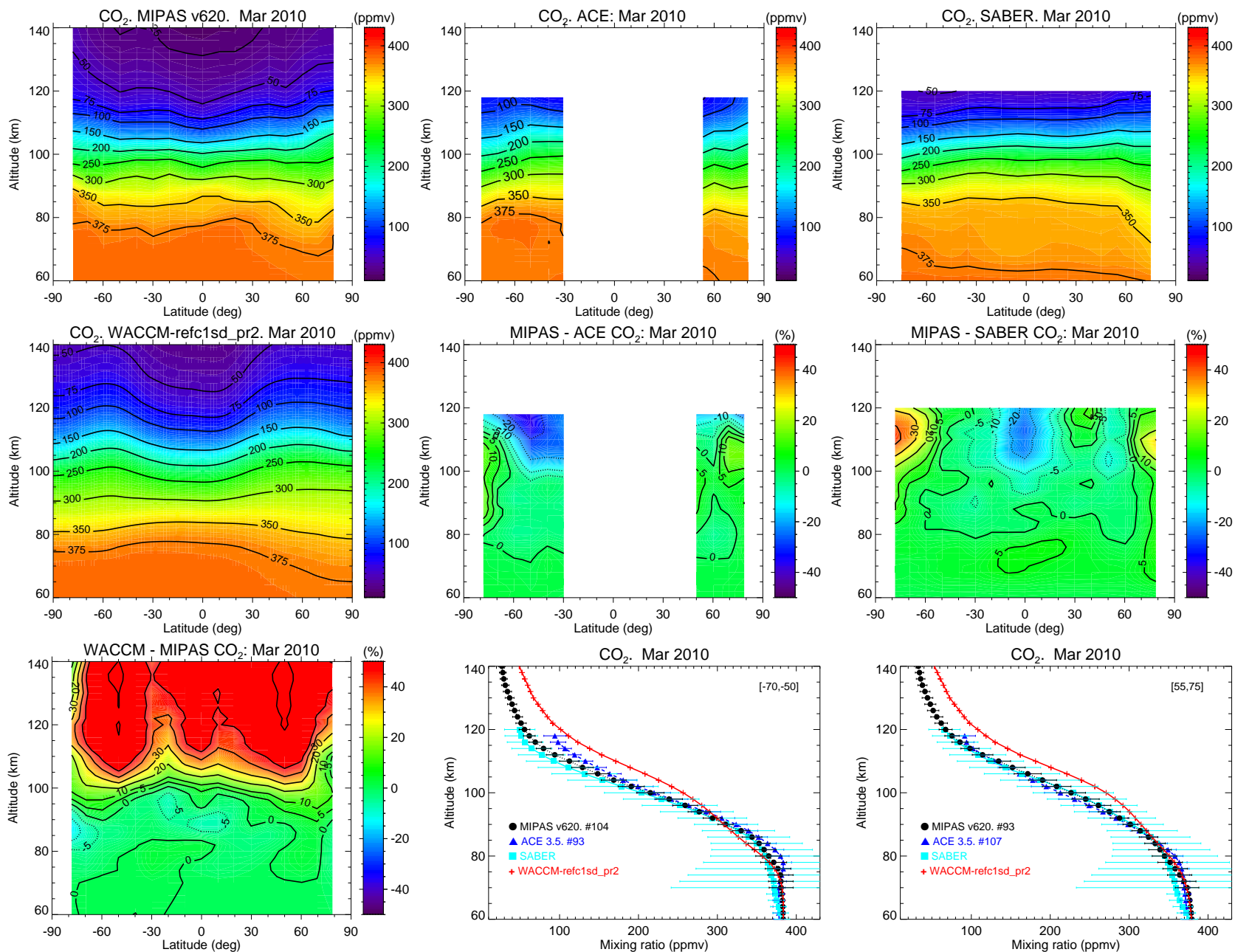


Figure 6.10: CO<sub>2</sub> vmr abundances for March 2010. Top row: zonal mean distribution of MIPAS, ACE and SABER, respectively. Middle row: SD-WACCM ( $P_r=2$ ) CO<sub>2</sub> distribution, and MIPAS-ACE and MIPAS-SABER CO<sub>2</sub> relative differences in %. Bottom row: WACCM-MIPAS CO<sub>2</sub> differences, and CO<sub>2</sub> vmr profiles for two latitude bands (as labelled) corresponding roughly to the ACE measurements. Horizontal bars in the measurements are the total errors, dominated by the systematic errors.

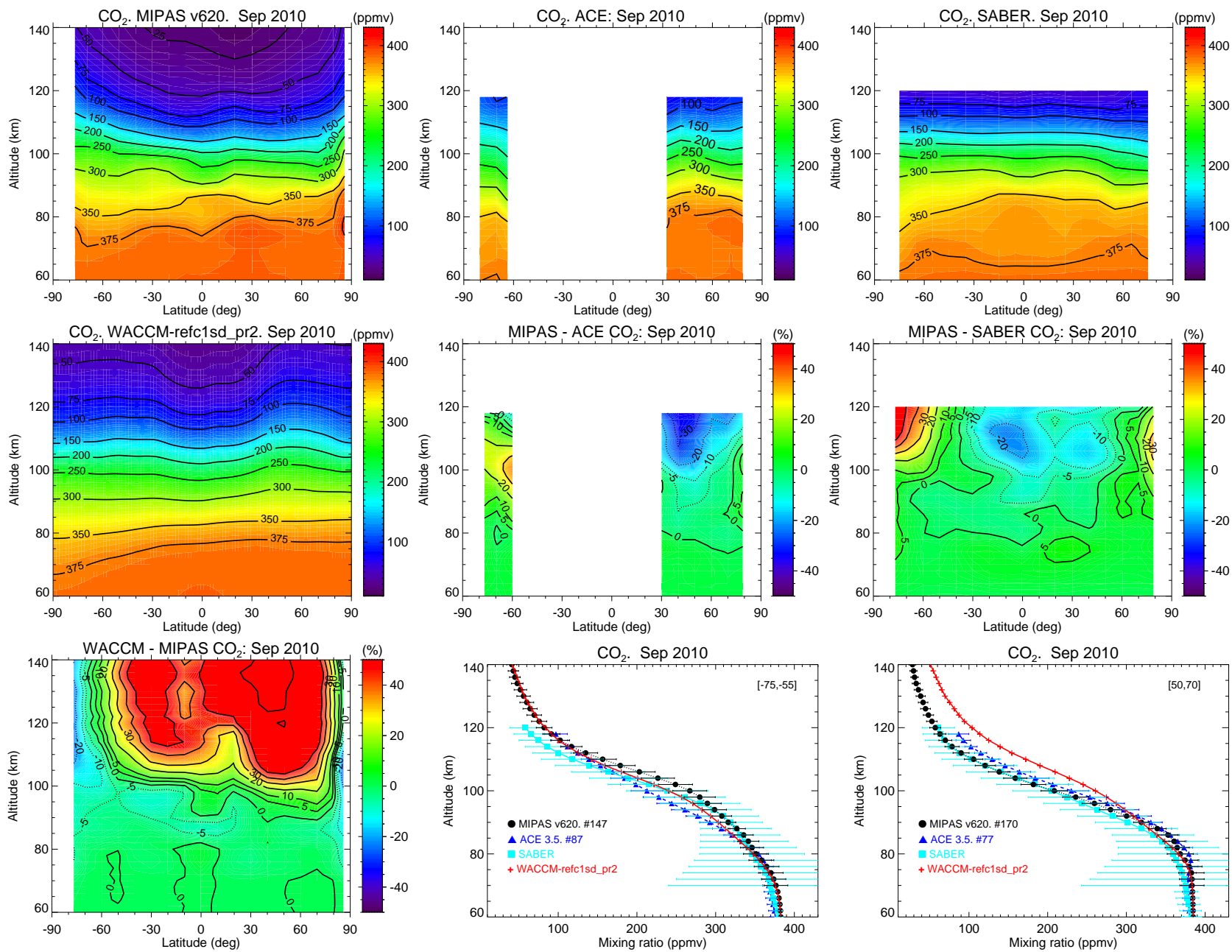


Figure 6.11: As Fig. 6.10 but for September 2010. Note that the latitude bands in the profiles panels are different.



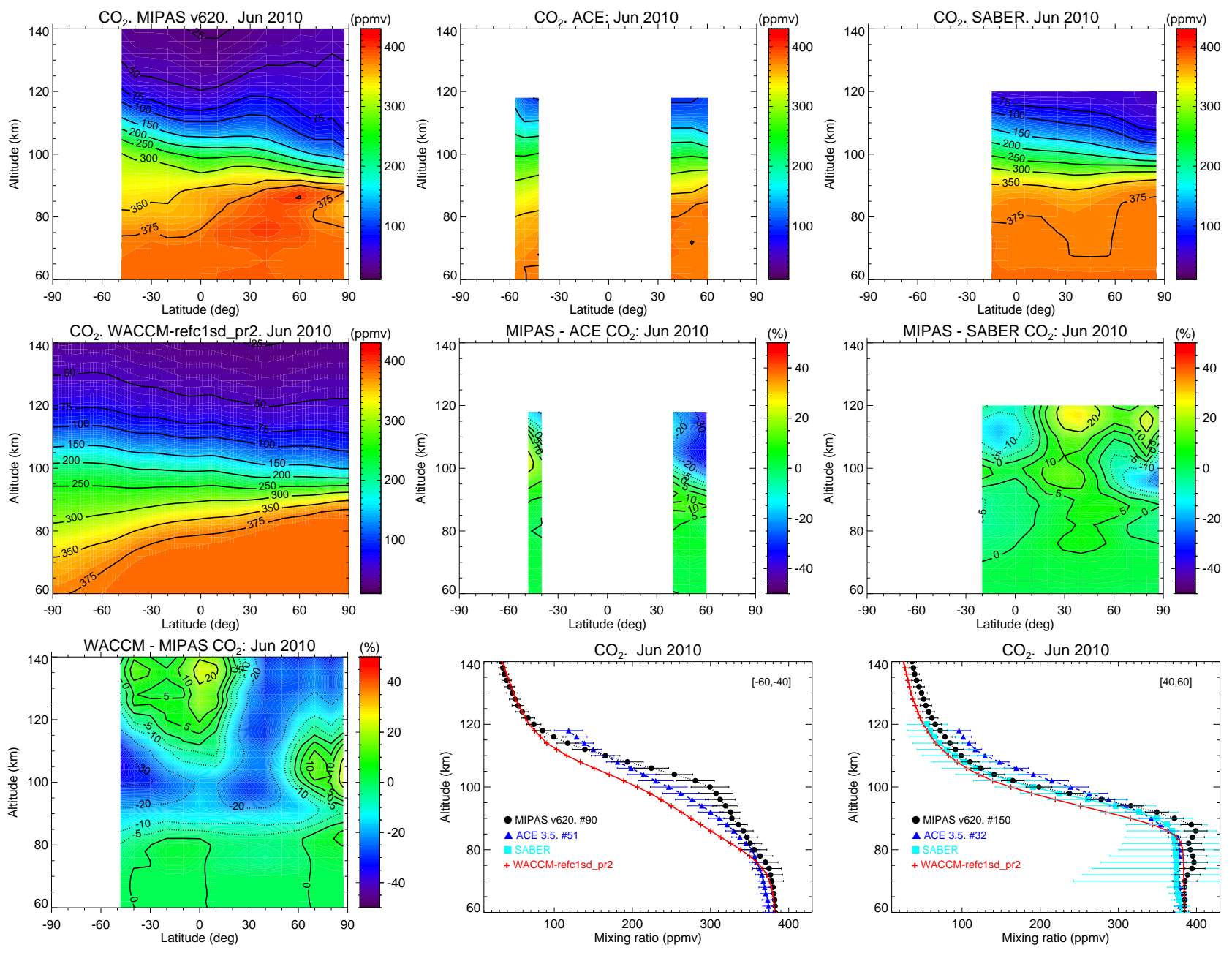


Figure 6.12: As Fig. 6.10 but for June 2010. Note that the latitude bands in the profiles panels are different.

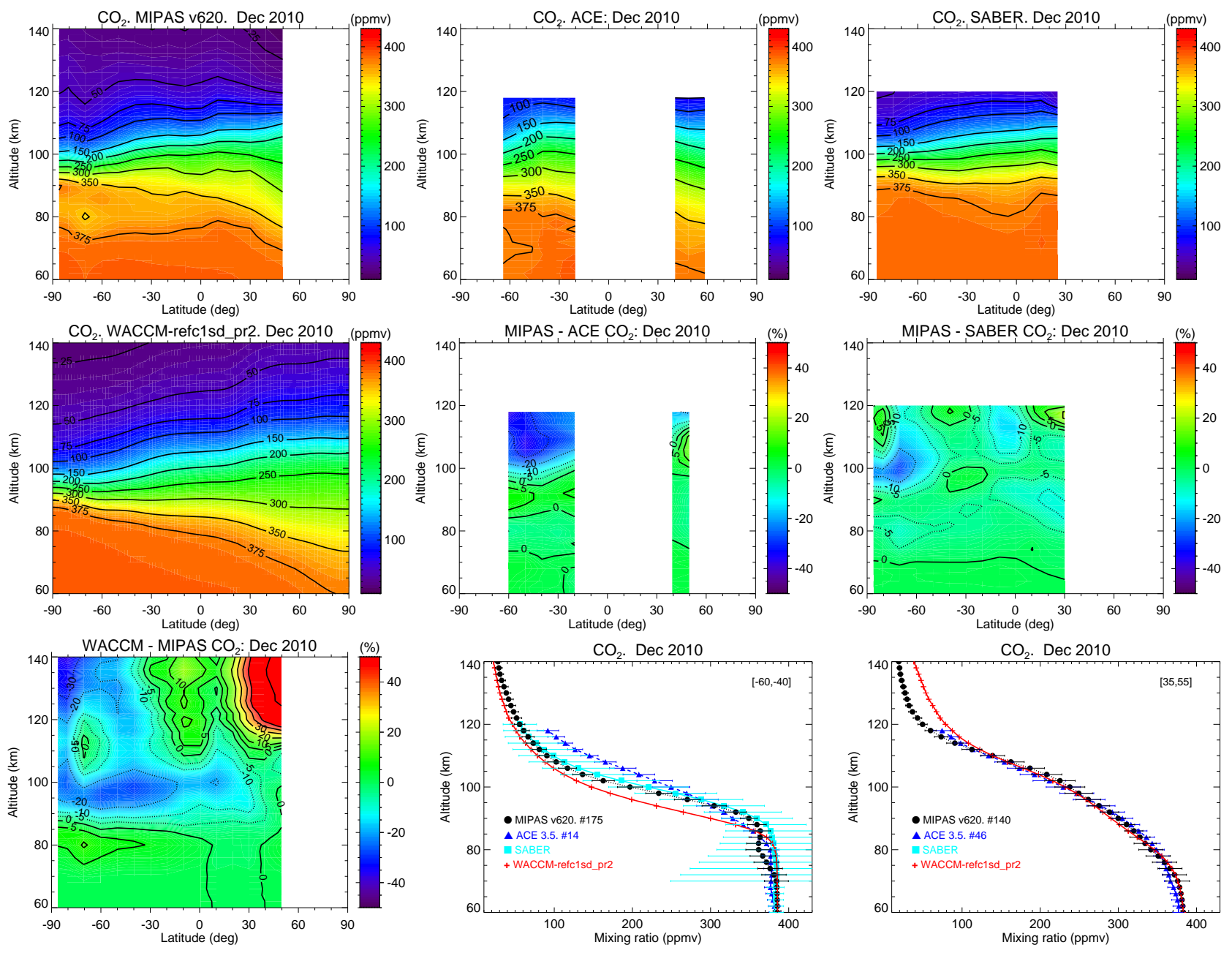


Figure 6.13: As Fig. 6.10 but for December 2010. Note that the latitude bands in the profiles panels are different.

The agreement of MIPAS with ACE is similar as for equinox conditions, but there is a clear difference in the polar summer (see Fig. 6.13, middle panel of bottom row; also seen in January, see Fig. C.1 in Appendix C), where the decay of the CO<sub>2</sub> vmr with altitude above ~100 km is steeper in MIPAS than in ACE. Actually this behavior is also present in SABER (in excellent agreement with MIPAS) and also predicted by WACCM. The model predicts, however, a CO<sub>2</sub> vmr which is too low at 40-60°S (middle panel, bottom row) (more clearly seen in January, see Fig. C.1). The agreement of MIPAS with SABER is in general very good. See, for example, the vertical profiles panels in Figs. 6.12 and 6.13, where, with the exception of June at 60°S-40°S, the profiles are practically identical above ~90 km. MIPAS CO<sub>2</sub> is, however, low compared to ACE (~5%) around 80 km in the polar summer (see Fig. 6.13 and also in Fig. C.1 in Appendix C). On the other hand, for mid-high latitudes in the summer hemisphere, MIPAS is sometimes rather large (~5%) at 80-90 km (see Fig. 6.12, bottom right panel, although the CO<sub>2</sub> vmr in this case is the largest we have obtained for any month in the 2010-2011 period, see Appendix C).

The agreement between MIPAS and SABER CO<sub>2</sub> in the 60-90 km region is sometimes not so good in the polar summer. This is more evident for January at high latitudes (Figs. C.1 and C.13, bottom right panels), although this seems to be due to an unrealistically low CO<sub>2</sub> abundance of SABER since this is much lower than MIPAS, ACE and WACCM there. In February, however, SABER shows an unrealistically high CO<sub>2</sub> vmr at these altitudes and latitudes (see, e.g., Fig. C.2).

In order to draw more general conclusions about the consistency among the three instruments and WACCM we have compared zonal mean cross-section and latitudinal band profiles for the annual mean of 2010 (see Figs. 6.14 and 6.15). When comparing MIPAS with ACE (bottom left panel of Fig. 6.14), it is evident that MIPAS CO<sub>2</sub> is generally higher by ~5% between 80 and 100 km but 20-30% lower between 100 and 120 km. MIPAS and SABER, however, agree very well up to 100 km. At 100-120 km, they also agree very well when averaging over all latitudes, but MIPAS CO<sub>2</sub> is generally higher than SABER except near the equator where MIPAS is lower. That is, in the 100-120 km region, globally, ACE shows the highest CO<sub>2</sub>, SABER the lowest and MIPAS is in between. Comparing MIPAS with WACCM (see also below), we see a general underestimation by WACCM ( $P_r=2$ ) of 5-10% at 80-100 km. The same is true for SABER. Part of this could be due to a positive bias in both MIPAS and SABER (both are larger than ACE) caused by and the retrieval of CO<sub>2</sub> in limb emission (MIPAS and SABER) sometimes gives unrealistically large CO<sub>2</sub>, see above and also the top panels in Fig. 6.15). However, even though WACCM seems to be a bit low (see lower panel of Fig. 6.15 for the 60°S-60°N latitudinal band). We should mention that increasing the Prandtl number to  $P_r=4$  would worsen the agreement, hence suggesting that  $P_r=2$  seems to be more appropriate at these altitudes.

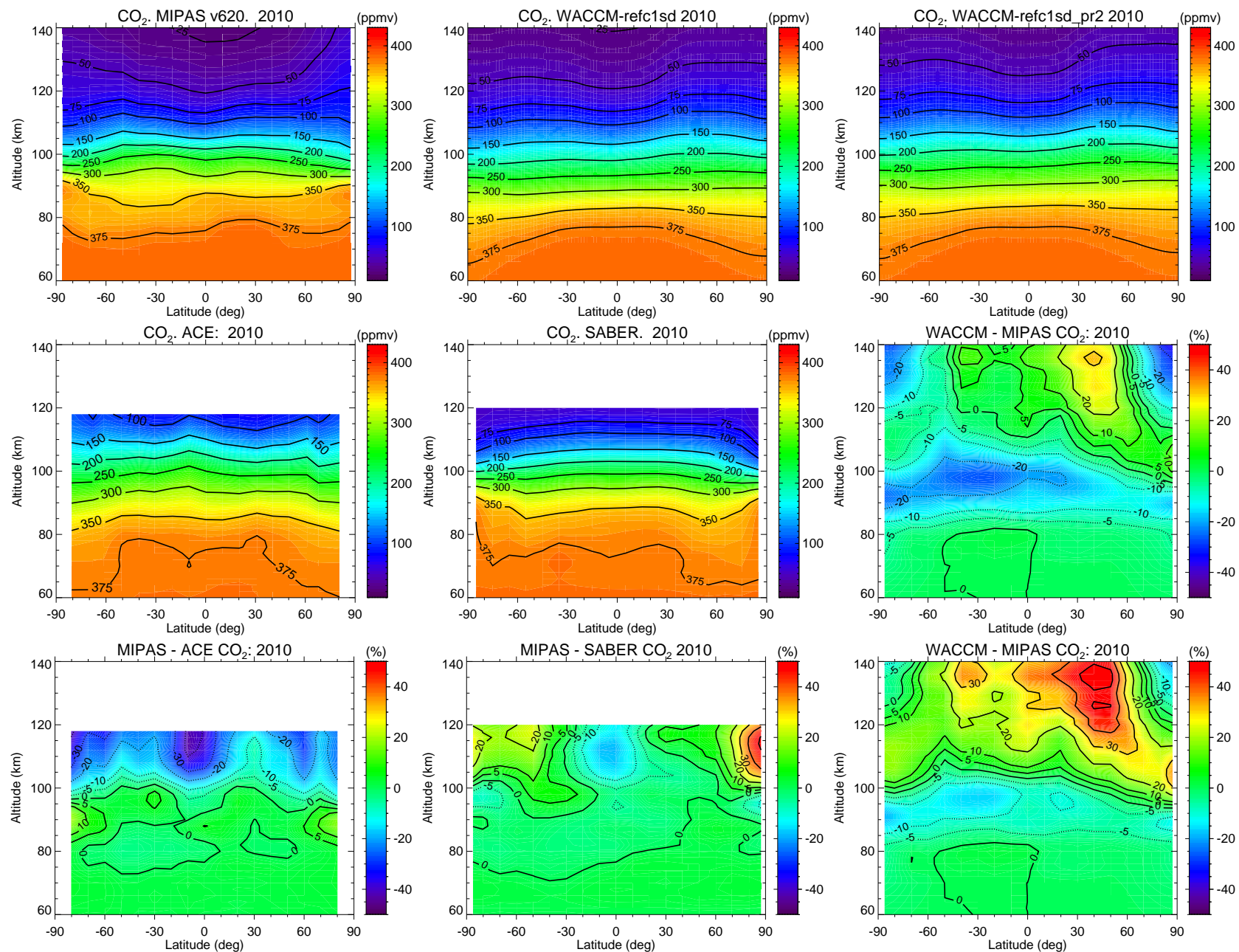


Figure 6.14: Annual mean CO<sub>2</sub> vmr abundances for 2010. Top row: zonal mean distribution of MIPAS, and WACCM ( $P_r=4$ ) and WACCM ( $P_r=2$ ), respectively. Middle row: zonal mean distribution of CO<sub>2</sub> for ACE and SABER; and WACCM( $P_r=4$ )-MIPAS differences, respectively. Bottom row: Differences of MIPAS-ACE, MIPAS-SABER, and WACCM( $P_r=2$ )-MIPAS, respectively.



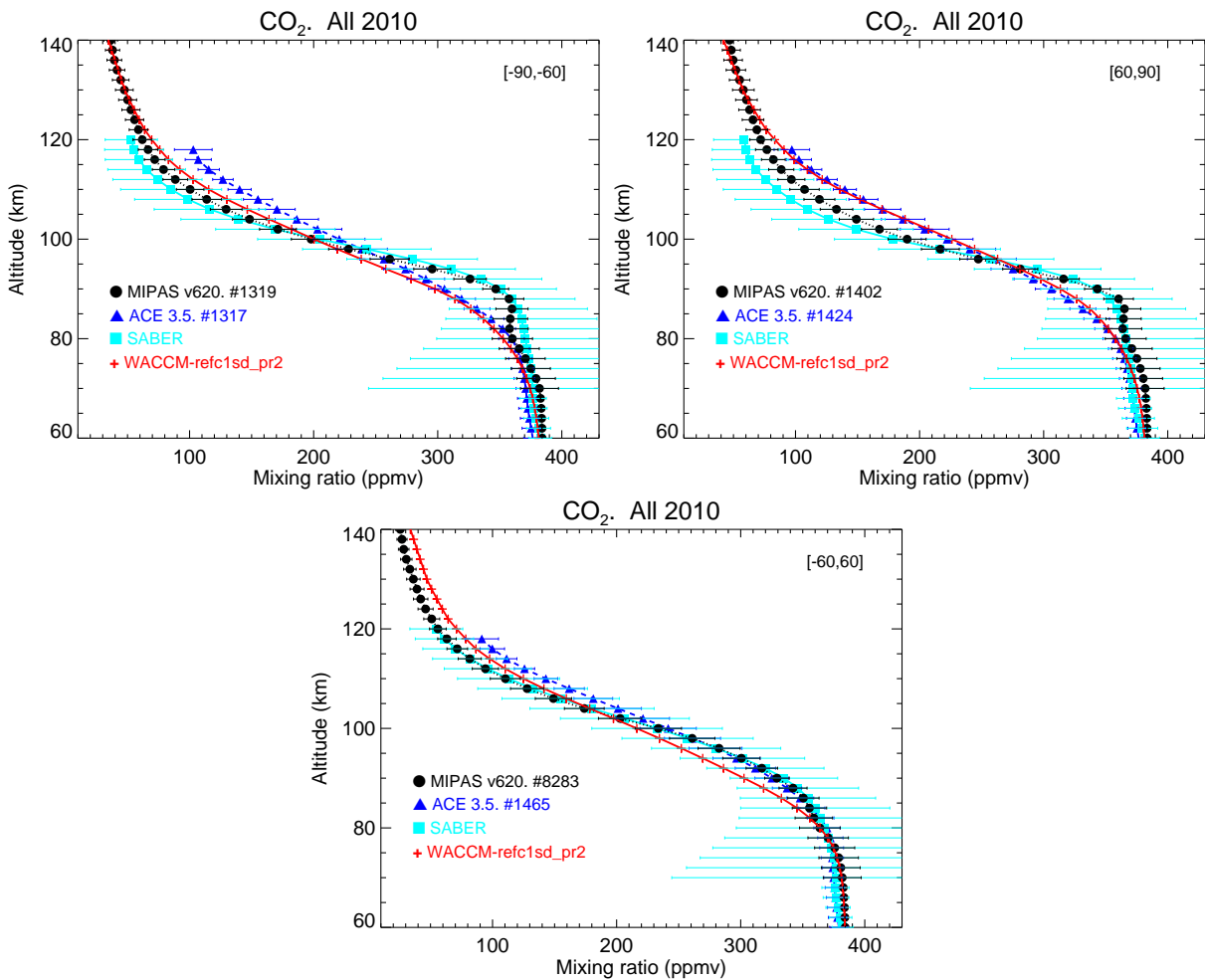


Figure 6.15: Annual mean CO<sub>2</sub> vmr abundances for 2010. Profiles for the Southern polar region (90°S-60°S) (top, left); Northern polar region (60°N-90°N) (top, right); and mid-latitudes and tropics (60°S-60°N) (bottom).

Between 100 and 120 km MIPAS CO<sub>2</sub> is slightly smaller than WACCM ( $P_r=2$ ), and significantly smaller than ACE. Hence the CO<sub>2</sub> mixing ratio simulated by WACCM lies between that observed by MIPAS and ACE and slightly closer to the former. Inspecting in detail the ACE CO<sub>2</sub> retrieval we observe that above around 110 km the CO<sub>2</sub> vmr unrealistically increases with altitude in quite a few of the scans. This might introduce a positive bias which might be responsible for the ACE larger values in this region. SABER measurements in this altitude region are globally smaller than MIPAS, ACE and WACCM. WACCM simulations with  $P_r=4$  somehow mitigates the WACCM  $P_r=2$  overestimations and give an overall better agreement with MIPAS in the 100-120 km region and above (see Fig. 6.14, middle-right panel). In the uppermost region, 120-140 km, the WACCM-MIPAS differences show a rather strong latitudinal variation, with WACCM underestimating the CO<sub>2</sub> in the polar regions and overestimating it in the tropics and mid-latitudes. That also occurs even when decreasing the eddy diffusion coefficient ( $P_r=4$ ) (see Fig. 6.14, middle column, right panel).

## 6.7. Comparison with WACCM Simulations

The Whole Atmosphere Community Climate model (WACCM) has been recently updated with the chemistry of CO and CO<sub>2</sub>, as well as the eddy diffusion term, and has been recently compared to ACE CO and CO<sub>2</sub> measurements and MIPAS CO abundances (Garcia et al., 2014). Since this is one of the most complete models of the middle and upper atmosphere we compared the MIPAS CO<sub>2</sub> with the WACCM predictions for several input parameters in order to learn about the dynamics and chemistry of the upper atmosphere. A brief comparison has been done in the previous section. Here we show a more detailed comparison with two WACCM simulations for the standard Prandtl number of  $P_r = 4$  and a smaller value of  $P_r = 2$ , which is equivalent to increasing the eddy diffusion coefficient  $k_{zz}$  by a factor of 2. The zonal mean CO<sub>2</sub> WACCM–MIPAS differences for all months of 2010 are shown in Figs. 6.16 and 6.17 for WACCM( $P_r = 4$ ) and WACCM( $P_r = 2$ ), respectively; and Fig. 6.18 shows CO<sub>2</sub> profiles and differences for three latitude bands for March, September, June and December of 2010. Similar figures have been produced by representing the CO<sub>2</sub> fields versus pressure (not shown) but they exhibit essentially the same general features.

In general, MIPAS is more consistent with a value of  $P_r=2$  (larger eddy diffusion) in WACCM predictions in the 80-100 km region. These model simulations give an overall better agreement at practically all latitudes and seasonal conditions (see Fig. 6.18).

Above 100 km, examination of Figs. 6.16 and 6.17 shows that WACCM overestimates the MIPAS CO<sub>2</sub> at equinox at practically all latitudes. However, at mid- and high-latitudes in the summer hemisphere WACCM in general under-predicts the CO<sub>2</sub> distribution. Since the overall effect of decreasing the Prandtl number (increasing the eddy diffusion) is to increase the CO<sub>2</sub> concentration above around 80-90 km, we then have a better agreement between MIPAS and WACCM for solstice conditions (suggesting a larger eddy diffusion,  $P_r=2$ ), particularly at mid- and high-latitudes in the summer hemisphere. On the contrary, at equinox conditions at almost all latitudes, and for solstice conditions at mid- to high latitudes in the winter hemisphere a smaller eddy diffusion seems to give a better agreement.

Of course there could be other reasons that explain those differences. For example, a weaker residual circulation in the lower thermosphere would lead to less efficient downwards transport of the CO<sub>2</sub>-poor air from high altitudes into the polar summer lowermost thermosphere and hence produce a larger CO<sub>2</sub> concentration there. About the larger WACCM concentration at equinox for most latitudes another possible reason could be an underestimation of the photochemical losses of CO<sub>2</sub> in the model.

Overall, WACCM reproduces the major CO<sub>2</sub> vertical distribution patterns and the seasonal and latitudinal variations observed in MIPAS data. Below about 100 km the agreement is very good, with differences generally smaller than  $\pm 10\%$  (for  $P_r = 2$ ) except for solstice conditions when they can be as large as 20% being WACCM smaller. In the polar summer MIPAS is generally smaller at these altitudes by up to 5%, which might point to a problem in the retrieval. At 100-140 km

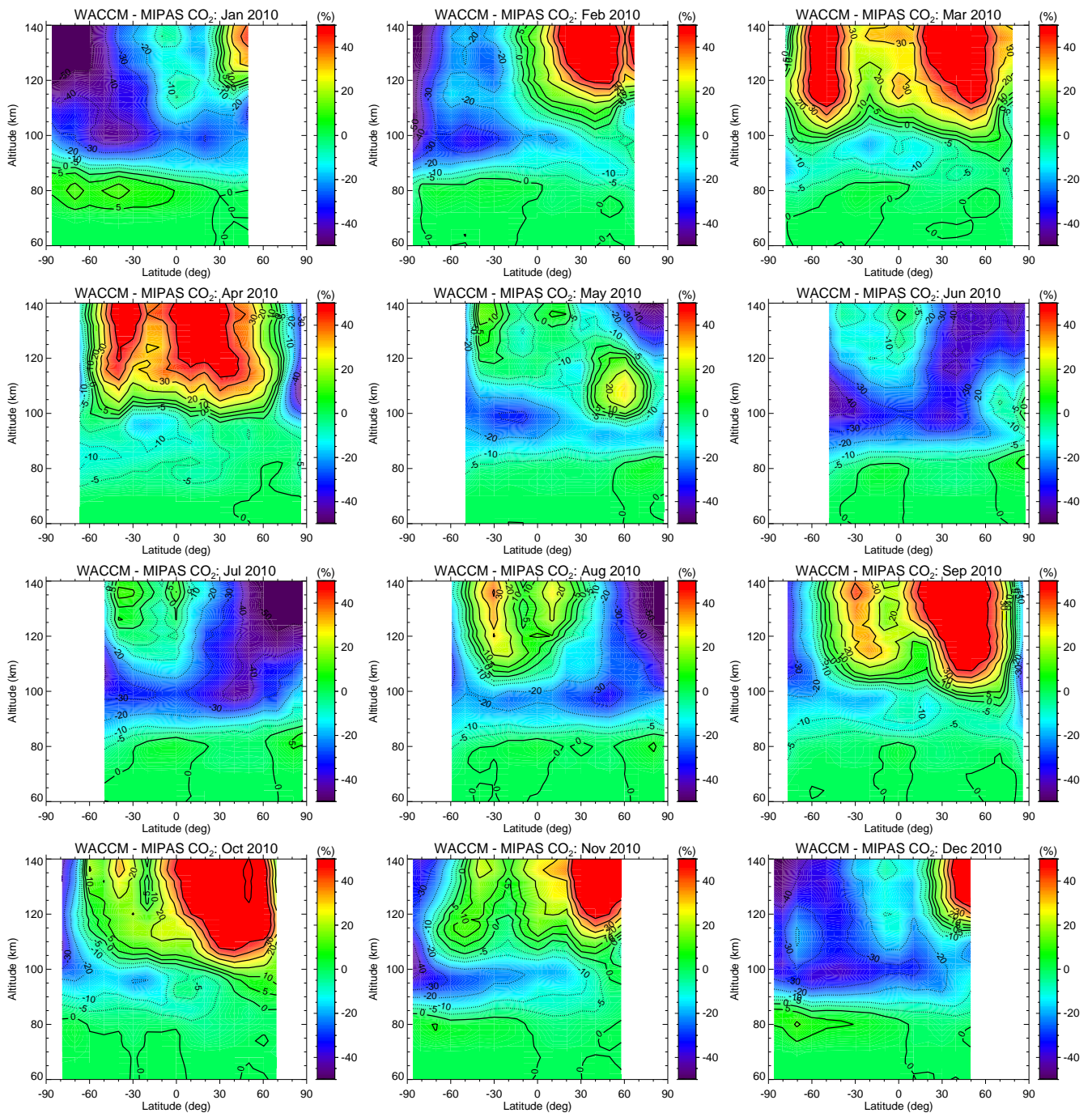


Figure 6.16: Monthly zonal mean CO<sub>2</sub> vmr WACCM( $P_r=4$ )-MIPAS differences for 2010.



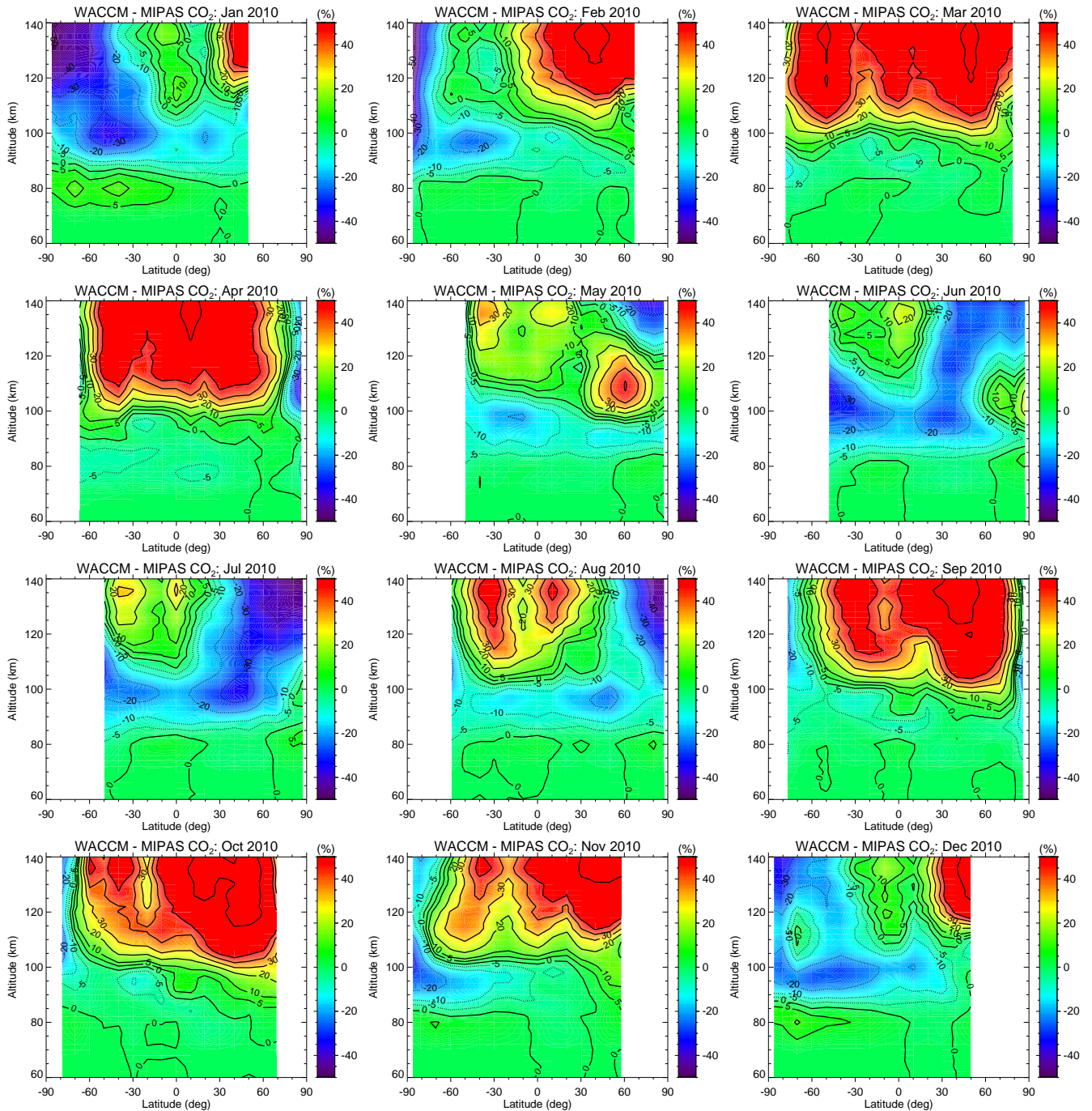


Figure 6.17: Monthly zonal mean CO<sub>2</sub> vmr WACCM( $P_r=2$ )-MIPAS differences for 2010.

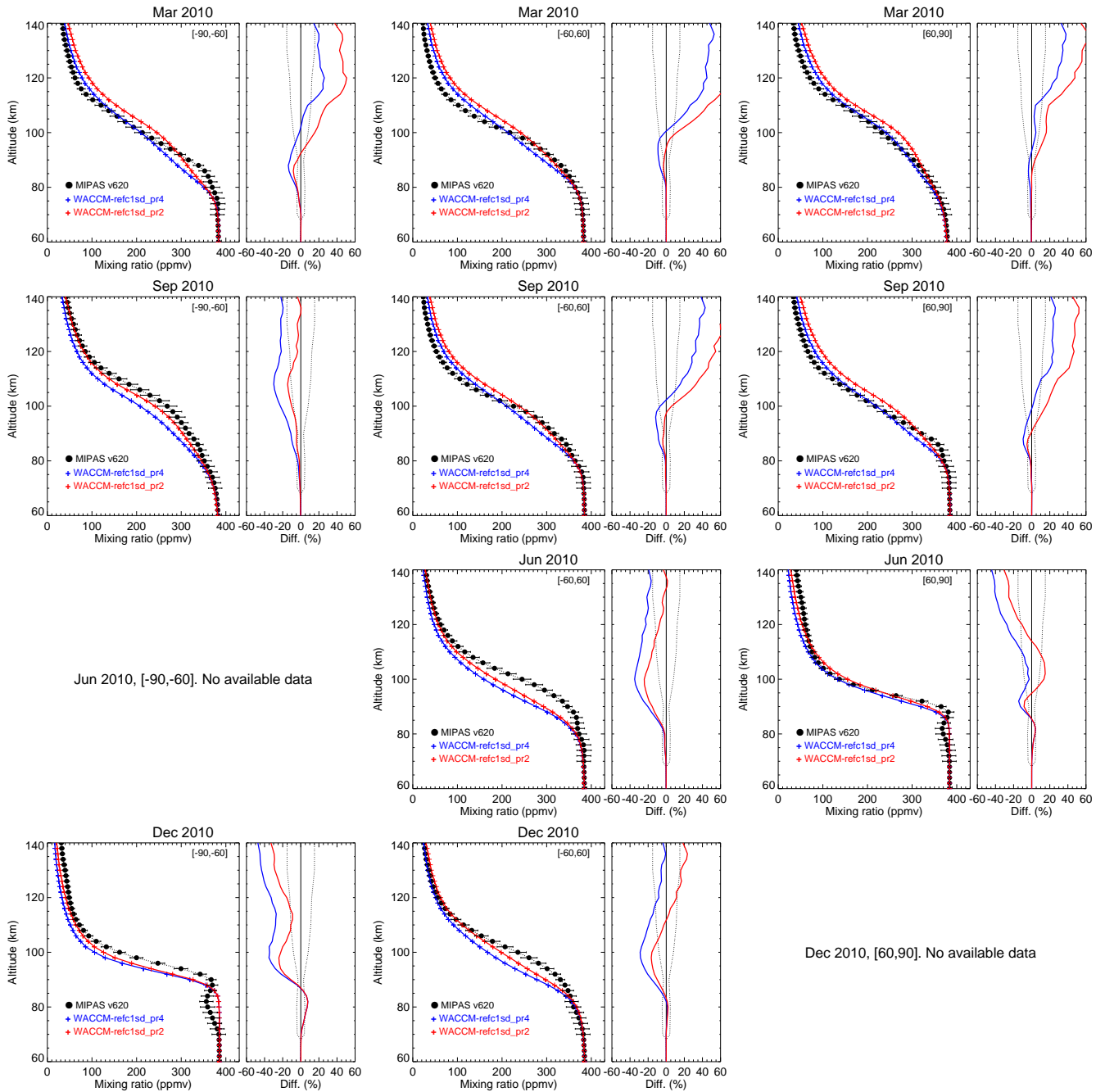


Figure 6.18: Comparison of MIPAS CO<sub>2</sub> with SD-WACCM simulations for  $P_r=4$  (standard) and  $P_r=2$  for March, September, June and December (rows 1-4) of 2010 for the Southern Hemisphere (90°S-60°S) (left column), mid-latitudes and tropics (60°N-60°S) (middle column) and Northern Hemisphere (60°N-90°N) (right column). Empty panels means no available MIPAS data. The right-hand panels show the WACCM-MIPAS differences, and the dotted lines represent the MIPAS total (mainly systematic) errors.

altitudes, WACCM CO<sub>2</sub> is generally larger than MIPAS at equinox at almost all latitudes with differences of 20-100%. In the summer hemispheres, however, WACCM CO<sub>2</sub> is generally lower in 20-70%. In the winter hemispheres WACCM CO<sub>2</sub> is also generally larger than MIPAS although not as large as in equinox. In general, MIPAS favors more a value of  $P_r = 2$  (larger eddy diffusion), principally below around 100 km. This WACCM/MIPAS comparison give rise to new questions (it should be bear in mind that no global measurement of CO<sub>2</sub> in the lower thermosphere were taken before MIPAS). For example, if the different CO<sub>2</sub> seasonal/latitudinal distributions could be explained by a seasonal/latitudinal dependence of the eddy diffusion,  $k_{zz}$ ; or if the lower thermosphere meridional circulation in WACCM is too strong. Also a possible reason for the discrepancies could be due to an underestimation of the photochemical losses of CO<sub>2</sub> in WACCM.

## 6.8. Inter-Annual Variability

MIPAS took measurements of the middle and upper atmosphere from January 2005 until April 2012. Hence it provides some information about the inter-annual variability of CO<sub>2</sub> in this region. The data from the Middle Atmosphere (MA) mode have not been processed yet. The inversion of CO<sub>2</sub> for this mode is more difficult and would be less accurate because we are missing the information of the CO<sub>2</sub> column above 100 km. Also, only 2 years of Upper Atmosphere (UA) mode data have been processed, because the most recent version of the thermospheric temperature, retrieved from the NO 5.3  $\mu\text{m}$  emission with the same setup as that used here, is currently not available. However, even having only 2 consecutive years of CO<sub>2</sub> data we have looked at the change between these two years. The results are shown in Fig. 6.19 for the bulk of the atmosphere comprised between 60°S to 60°N. The figure shows that MIPAS CO<sub>2</sub> decreases from 2010 to 2011 above around 100 km, as expected for the larger solar activity (larger EUV flux) for 2011 than for 2010. Note that the MIPAS result is consistent with the WACCM prediction and with the SABER measurements. ACE also shows an incipient decrease between 95 and 110 km, that turns into an increase above 110 km. This anomalous increase might be due to the general overestimation of CO<sub>2</sub> by ACE with respect to MIPAS and SABER above 110 km, which, as discussed above might not be realistic but due to a retrieval artifact and might change from year to year.

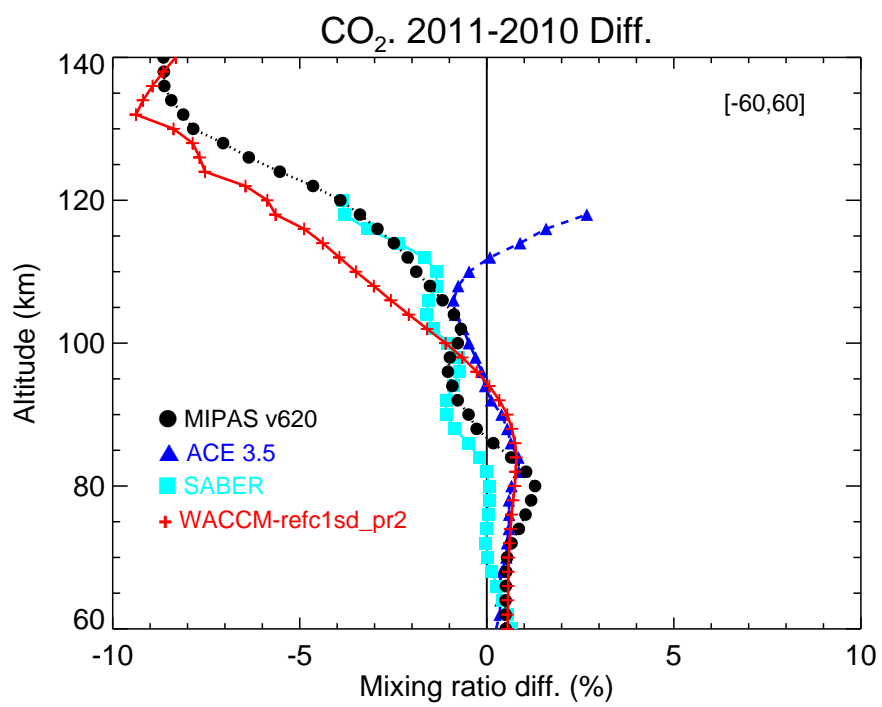


Figure 6.19: Inter-annual variation (2011–2010 differences) of CO<sub>2</sub> vmr from 2010 to 2011 for tropics and mid-latitudes.





## Chapter 7

# Conclusions and Future Work

### *Abstract*

In this chapter we present the general conclusions from the results of this work. We have analyzed here MIPAS UA measurements from the mesosphere up to the middle thermosphere. First, we make the most of the MIPAS high spectral resolution and wide altitude range to derive new values for the most important vibration-vibration and vibration-thermal collisional rates affecting to the populations of the CO<sub>2</sub> levels emitting in the mid- and near-IR. These have an unprecedented accuracy and have a large impact on atmospheric spectral radiances in the 10, 4.3 and 2.7 μm spectral regions, and, therefore, on the CO<sub>2</sub> retrieval from measurements of these emissions. Secondly, by using these results, we have retrieved global distributions of the CO<sub>2</sub> vmr (volume mixing ratio) in the mesosphere and middle thermosphere (up to 142 km) for 2010 and 2011. This is the first time that the relative CO<sub>2</sub> concentration (vmr) has been retrieved in the middle thermosphere (120-140 km). Furthermore, the retrieved CO<sub>2</sub> has an unprecedented accuracy because of the new rate coefficients derived and the simultaneous measurements of other key atmospheric parameters (temperature in the mesosphere and in the thermosphere, as well as O<sub>3</sub>) offered by the MIPAS spectra. A brief description of potential future work is also presented.

### 7.1. Non-LTE Collisional Rates

In this section we summarize the results on the retrieved collisional rates from MIPAS 10 and 4.3 μm spectra. MIPAS has a high spectral resolution (0.0625 cm<sup>-1</sup>) and a wide spectral coverage (from 685 to 2410 cm<sup>-1</sup>) that allow measuring and discriminating among the many bands contributing to the atmospheric limb radiance near 4.3 μm. Further, MIPAS has a high sensitivity that allows measuring this atmospheric emission in a wide altitude range, from 20 to ~170 km. Hence, MIPAS spectra provide unique information on the non-LTE populations of the many CO<sub>2</sub> levels emitting in the 4.3 μm region and on the processes that control them.

A sensitivity study was performed and showed that MIPAS spectra contain significant information on the following collisional rates:

a)  $k_{vv,2}$ ,  $k_{vv,3}$  and  $k_{vv,4}$ :  $\text{CO}_2(v_d, v_3) + \text{N}_2 \rightleftharpoons \text{CO}_2(v_d, v_3-1) + \text{N}_2(1)$  with  $v_d = 2v_1 +$

$v_2=2$ ,  $v_d=3$ , and  $v_d=4$ , respectively;

- b)  $k_{F1}$  and  $k_{F2}$ :  $\text{CO}_2(v_1, v_2, l, 1, r) + \text{M} \rightleftharpoons \text{CO}_2(v'_1, v'_2, l', 1, r') + \text{M}$  with  $\Delta v_d=0$  and  $\Delta l=0$  ( $k_{F1}$ ), and with  $\Delta v_d=0$ ,  $\Delta l \neq 0$  ( $k_{F2}$ );
- c)  $k_{vt}$ , the thermal relaxation of  $\text{CO}_2(v_3)$  to the  $v_1$  and  $v_2$  modes, e.g.,  $\text{CO}_2(v_d, v_3) + \text{M} \rightleftharpoons \text{CO}_2(v'_d, v_3-1) + \text{M}$  with  $\Delta v_d=2-4$  and  $\Delta v_3=-1$ ; and
- d) The efficiency of the excitation of  $\text{N}_2(1)$  by  $\text{O}(^1D)$ .

A non-LTE retrieval scheme, used in previous analysis of the MIPAS non-LTE emission, has been applied to the MIPAS 10 and 4.3  $\mu\text{m}$  spectra. The collisional rates listed above, together with the  $\text{CO}_2$  vmr, have been retrieved from four days of MIPAS measurements (17 January, 30 March, 8 June and 26 September of 2010) taken in its 'Upper Atmosphere' mode, covering solstice and equinox conditions and pole-to-pole latitudes. The wide altitude and latitude ranges have allowed to retrieve also the temperature dependence of the collisional rates in the range of 130 to 250 K. The values obtained together with their temperature dependence and errors are shown in Table 5.1. All of them were retrieved with a much better accuracy that known before. The most salient results are:

- The  $k_{vv,2}$  derived here has a stronger temperature dependence than that used before. Also, it is significantly larger than previous values at temperatures below 300 K, ranging from a factor of 1 to 1.5 from 300 K to 130 K. This is a result of major importance since this rate controls the populations of the  $\text{CO}_2(10011)$  and  $(10012)$  levels, and therefore the atmospheric radiation near 4.3  $\mu\text{m}$  and 2.7  $\mu\text{m}$  at upper mesospheric and lower thermospheric limb paths.
- The collisional rates for the V-V transfer from high energy levels,  $k_{vv,3}$  and  $k_{vv,4}$ , have been retrieved here for the first time. We have retrieved a temperature dependence of  $1/T^{0.6}$ , slightly stronger than  $1/\sqrt{T}$ , with values larger than previous rates by about 20% at mesospheric temperatures. We have not found any significant difference between  $k_{vv,3}$  and  $k_{vv,4}$ .
- We have retrieved values for the  $k_{F1}$  and  $k_{F2}$  rates very different from those previously used.  $k_{F1}$  is about 43 times smaller than the rate derived by Sharma and Wintersteiner (1985) and about 4.7 times larger than that used by Shved et al. (1998).  $k_{F2}$  is about a factor of 9 to 5 (4.5 to 2.5 for  $k_{F2'}$ ) larger than those used by Sharma and Wintersteiner (1985) and Shved et al. (1998) for temperatures of 150 and 250 K, respectively; and a factor of 2 to 3.5 (4 to 7 for  $k_{F2'}$ ) smaller for the same temperature interval than those included in López-Puertas and Taylor (1989) and López-Puertas et al. (1998b). This leads to significant changes in the modeled atmospheric radiation of the two stronger 4.3  $\mu\text{m}$  second hot bands, decreasing them by 20-30% for mid-latitude conditions.
- The derived  $k_{vt}$  collisional rate is smaller (factor of 0.7) than the values used recently by Funke et al. (2012). It is also smaller by factors of 0.38 and 0.57

at 150 and 250 K than those used in the analysis of SPIRE, SAMS and ISAMS measurements; and by factors of 0.71 and 0.65 than those used by Shved et al. (1998) and incorporated in the analysis of CRISTA and SABER measurements. The  $k_{O(^1D)}$  collisional rate derived here jointly with  $k_{vt}$ , is very similar to that used by Funke et al. (2012). This means that it is factors of 1.5 and 1.1 (at 150 and 250 K, respectively) larger than those used in the analysis of SPIRE, SAMS and ISAMS measurements; and a factor of 1.21 larger than those used by Shved et al. (1998) and incorporated in the analysis of CRISTA and SABER measurements.

The new rates have very important effects on the atmospheric limb spectral radiances in the 10, 4.3 and 2.7  $\mu\text{m}$  spectral regions when compared to typical collisional rates used in previous works. They also lead to a reduction of the integrated radiance in the 2280-2400  $\text{cm}^{-1}$  range of 2-4% at tangent heights below  $\sim 85$  km for mid-altitudes conditions, and as large as 8% for polar summer. This reduction is expected to be even larger in the 2.7  $\mu\text{m}$  region. Also, a significant increase is expected in the 10  $\mu\text{m}$  laser bands. Thus, these new rates allows a more accurate inversion of the CO<sub>2</sub> vmr in the mesosphere and lower thermosphere from measurements taken in the 10, 4.3 and 2.7  $\mu\text{m}$  regions.

## 7.2. CO<sub>2</sub> Global Distributions in the Mesosphere and Thermosphere

In this section we summarize the major results of the CO<sub>2</sub> vmr distribution. Using the collisional rates describe above, we have retrieved global distributions of the CO<sub>2</sub> vmr in the mesosphere and thermosphere (up to  $\sim 140$  km) for 2010 and 2011. This is the first time that the relative CO<sub>2</sub> concentration (vmr) have been retrieved in the middle thermosphere (120-140 km). Furthermore, the retrieved CO<sub>2</sub> has an unprecedented accuracy because of the new rate coefficients derived and the simultaneous measurements of other key atmospheric parameters (temperature in the mesosphere and in the thermosphere, as well as O<sub>3</sub>) offered by the MIPAS spectra.

The CO<sub>2</sub> vmrs have been retrieved using MIPAS daytime limb emission spectra from the 4.3  $\mu\text{m}$  region in its upper atmosphere (UA) mode (data version CO2\_620.0). The retrieved CO<sub>2</sub> covers from 70 km up to about 140 km. The inversion has been performed by using a non-LTE retrieval scheme developed at IAA/IMK. It takes the advantage of other (simultaneous) MIPAS measurements of atmospheric parameters, as the kinetic temperature (up to  $\sim 100$  km) from the CO<sub>2</sub> 15  $\mu\text{m}$  region, the thermospheric temperature from the NO 5.3  $\mu\text{m}$ , the O<sub>3</sub> measurements (up to  $\sim 100$  km), which allows a strong constrain of the O(<sup>1</sup>D) concentration below  $\sim 100$  km, and an accurate calculation of O(<sup>1</sup>D) above  $\sim 100$  km. The non-LTE model incorporates the accurate vibrational-vibrational and vibrational-translational collisional rates derived from the MIPAS spectra.

The precision of the retrieved CO<sub>2</sub> vmr profiles varies with altitude ranging from

~1% below 90 km, to 5% around 120 km and larger than 10% above 130 km. The larger values at higher altitudes are due to the lower signal-to-noise ratio. There are very little latitudinal and seasonal variations, which are driven by the solar illumination conditions.

The retrieved CO<sub>2</sub> profiles have a vertical resolution of about 5–7 km below 120 km, with an increase of up to 12 km at ~100 km, and between 10 and 20 km at 120–140 km.

Retrieval simulations performed with synthetic spectra have demonstrated that the developed retrieval scheme allows to reproduce the CO<sub>2</sub> profile in the 70–140 km range with very high accuracy. Even when using strongly perturbed a priori information, deviations from the “true” profile are less than 4% for mid-latitude and 6% for polar summer conditions. The major systematic error source is the uncertainty (bias) of the pressure/temperature profiles which are retrieved in a preceding step. They can induce a systematic error up to 15–16% above 100 km and, at mid-latitude conditions, of 5% around 80 km. The systematic errors due to uncertainties of the O(<sup>1</sup>D) and O(<sup>3</sup>P) profiles are within 3–4% in the 100–120 km region. Finally, the errors due to uncertainties of the gain calibration and the solar flux at 4.3 and 2.7 μm are within ~2% at all altitudes.

The most important features observed on the retrieved CO<sub>2</sub> can be summarized in:

- The retrieved CO<sub>2</sub> shows the major general features expected and predicted by models: the abrupt decline of the CO<sub>2</sub> vmr above 80–90 km, caused by the predominance of the molecular diffusion, and the seasonal change of the latitudinal distribution. The latter is reflected by higher CO<sub>2</sub> abundances in polar summer from 70 km up to ~95 km, and lower CO<sub>2</sub> vmr in the polar winter, both induced by the ascending and descending branches of the meridional circulation, respectively. Above ~95 km, CO<sub>2</sub> is more abundant in the polar winter than at mid-latitudes and polar summer regions, caused by the reversal of the meridional circulation in that altitude region.
- The typical solstice and equinox latitudinal distributions are found in the data periods of about 2.5 months in each hemisphere, and the solstice/equinox seasonal transition usually takes place rather quickly, in about one month.
- We have found a small decrease in MIPAS CO<sub>2</sub> vmr at ~80 km at polar summer latitudes. We are not sure if this is real, e.g., remnant CO<sub>2</sub> air from previous season, or a retrieval artifact caused by a combination of high solar zenith angles and low temperatures.

With the aim of validating the retrieved MIPAS CO<sub>2</sub> vmr, a detailed comparison has been performed with the most recent satellite measurements taken by ACE and SABER. The major results can be summarized in:

- In equinox, MIPAS shows an overall good agreement with ACE. MIPAS CO<sub>2</sub> measurements are slightly larger than those of ACE at 80–100 km. At higher

altitudes, the differences varies with latitude, being comprised always within  $\pm 20\%$ .

- Also in equinox, the agreement of MIPAS with SABER is even better than with ACE, being within 5% below 100 km. In the 100-120 km region, MIPAS tends to be a  $\sim 20\%$  larger in polar regions and a  $\sim 10\text{-}20\%$  smaller near the tropics.
- During solstice there is, in general, a very good agreement between the CO<sub>2</sub> measurements of the three instruments. The agreement of MIPAS with ACE is similar as for equinox conditions, but there is a clear distinction in the polar summer, where the decay of the CO<sub>2</sub> vmr with altitude above  $\sim 100$  km is steeper in MIPAS than in ACE. This behavior is also present in SABER data (in excellent agreement with MIPAS) and is it is even more prominent (probably too steep) in WACCM simulations (see below).
- The agreement of MIPAS with SABER is in general very good. MIPAS CO<sub>2</sub> is, however, smaller ( $\sim 5\%$ , and probably too low) around 80 km in the polar summer. SABER, on the other hand, seems to be too low at 60–80 km in the polar winter in January, and too high at 65-95 km in the polar winter in February.
- WACCM generally overestimates the CO<sub>2</sub> of the three instruments above  $\sim 90$  km at mid- and tropical latitudes during equinox. However, the opposite occurs during solstice at mid and high latitudes of the summer hemisphere, when WACCM CO<sub>2</sub> decreases more pronouncedly than the CO<sub>2</sub> of the three instruments at those altitudes.

In order to draw more general conclusions we have also compared zonal mean cross-section and latitudinal band profiles for the annual mean of 2010. The results showed that:

- MIPAS measurements are generally larger ( $\sim 5\%$ ) than ACE ones at 80-100 km and 20-30% smaller at 100-120 km.
- MIPAS and SABER agree very well up to 100 km. At 100-120 km, they also agree very well when averaging over all latitudes, but MIPAS is generally larger than SABER except near the equator where MIPAS is lower. That is, in the 100-120 km region, globally, ACE is the largest, SABER the smallest and MIPAS is in between.
- SABER CO<sub>2</sub> measurements between 100 and 120 km are globally smaller than MIPAS, ACE and WACCM.

From the detailed comparison of WACCM simulations with MIPAS observations we draw the following conclusions:

- Overall, WACCM reproduces the major CO<sub>2</sub> vertical distribution patterns and the seasonal and latitudinal variations observed in MIPAS data.

- Below about 100 km the agreement is very good, with differences smaller than  $\pm 10\%$  (for  $P_r = 2$ ) except for solstice conditions near 90-100 km where they can be as large as 20%, being WACCM smaller. In the polar summer, near 80 km, MIPAS is smaller by up to 5%, which might point to a problem in the MIPAS CO<sub>2</sub> retrieval.
- At 100-140 km altitudes, WACCM CO<sub>2</sub> is generally larger than MIPAS at equinox at almost all latitudes with differences of 20-100%. In the summer hemispheres, however, WACCM CO<sub>2</sub> is generally lower in 20-70%. In the winter hemispheres WACCM CO<sub>2</sub> is also generally larger than MIPAS although not as large as in equinox.
- In general, MIPAS favors more a value of  $P_r = 2$  (larger eddy diffusion), principally below around 100 km. In the 100-120 km region and above, however, WACCM simulations with  $P_r=4$  somehow mitigates the WACCM  $P_r=2$  overestimations and give an overall better agreement with MIPAS.
- The WACCM/MIPAS comparison give rise to new questions. For example, can the different MIPAS/WACCM CO<sub>2</sub> seasonal/latitudinal distributions be explained by a seasonal/latitudinal dependence of the eddy diffusion?; or is the lower thermosphere residual circulation in WACCM too strong?; or are they caused by an underestimation of the photochemical losses of CO<sub>2</sub> in WACCM?

Finally, the MIPAS global (60°S–60°N) CO<sub>2</sub> vmr above  $\sim 100$  km showed a decrease in 2011 with respect to 2010, which is consistent with the larger solar activity of 2011. This result is also consistent with SABER measurements and WACCM predictions. ACE measurements show also a decrease from 95 km up to 110 km but not between 110 and 120 km.

### 7.3. Future Work

In a near future, the most urgent work will be to complete the CO<sub>2</sub> retrieval from the whole MIPAS optimized resolution upper atmosphere (UA) mode data set, from 2005 to the end of the Envisat mission in 2012. This will be done after the retrieval of the thermospheric temperature is available for those years. This CO<sub>2</sub> database will then cover nearly a complete solar cycle and, therefore, could be used to perform an inter-annual variability study. Of particular importance is to check if it shows also a trend of CO<sub>2</sub> in the middle and upper atmosphere larger than that expected from the CO<sub>2</sub> anthropogenic increase in the lower thermosphere, as has been recently reported from the ACE (Emmert et al., 2012) and SABER (Yue et al., 2015) measurements. MIPAS CO<sub>2</sub> measurements, although limited in time with respect to ACE and SABER, have the advantages of providing simultaneously and globally the CO abundance, and covering higher altitudes, up to 140 km. These would allow to study in detail the CO<sub>x</sub> chemistry and the dynamics of the middle thermosphere, practically an unexplored region.

Other potential work to be carried out in the future is the study of the upper atmosphere infrared cooling. SABER has measured (still measuring) the CO<sub>2</sub> and NO coolings, but could not derive the temperature and CO<sub>2</sub> and NO volume mixing ratios. MIPAS, however, is able to provide those measurements. Hence, comparison of the CO<sub>2</sub> and NO cooling rates calculated with the MIPAS products and those measured by SABER would be very valuable. Also, comparison with WACCM simulations would be very useful, since MIPAS offers important constraints as the temperature, and the CO, CO<sub>2</sub> and NO relative concentrations.

On the algorithm development side, it would be very useful to develop the "setups" for the retrievals of CO<sub>2</sub> from the middle atmosphere (MA) and Noctilucent Cloud (NLC) MIPAS observations modes. We do not expect to gain much information about the CO<sub>2</sub> distribution, since they cover essentially the same periods and latitudes, but would shed some light on the effect of the CO<sub>2</sub> column above 100 km, hence being of potential use for future retrievals with limited altitude coverage of the measurements.





## Appendix A

# Table of CO<sub>2</sub> Bands

Table A.1: Principal CO<sub>2</sub> bands emitting near 4.3 μm included in this work.

Iso <sup>◊</sup>	Band	Upper level <sup>†</sup>	Lower level <sup>†</sup>	$\tilde{\nu}_0^*$ (cm <sup>-1</sup> )	$A^\ddagger$ (s <sup>-1</sup> )
1	FB	(9) 00011 (00 <sup>0</sup> 1)	(1) 00001 (00 <sup>0</sup> 0)	2349.14	423.8
1	FH	(16) 01111 (01 <sup>1</sup> 1)	(2) 01101 (01 <sup>1</sup> 0)	2336.63	413.2
1	SH	(23) 10012 (02 <sup>0</sup> 1)	(3) 10002 (02 <sup>0</sup> 0)	2327.43	403.3
1	SH	(24) 02211 (02 <sup>2</sup> 1)	(4) 02201 (02 <sup>2</sup> 0)	2324.14	400.6
1	SH	(25) 10011 (10 <sup>0</sup> 1)	(5) 10001 (10 <sup>0</sup> 0)	2326.60	401.0
1	TH	(36) 11112 (03 <sup>1</sup> 1)	(6) 11102 (03 <sup>1</sup> 0)	2315.23	393.7
1	TH	(37) 03311 (03 <sup>3</sup> 1)	(7) 03301 (03 <sup>3</sup> 0)	2311.67	386.2
1	TH	(38) 11111 (11 <sup>1</sup> 1)	(8) 11101 (11 <sup>1</sup> 0)	2313.77	390.7
1	FH $v_3$	(39) 00021 (00 <sup>0</sup> 2)	(9) 00011 (00 <sup>0</sup> 1)	2324.18	413.6
1	FrH	(43) 20013 (04 <sup>0</sup> 1)	(10) 20003 (04 <sup>0</sup> 0)	2305.26	385.0
1	FrH	(44) 12212 (04 <sup>2</sup> 1)	(11) 12202 (04 <sup>2</sup> 0)	2302.97	380.4
1	FrH	(47) 04411 (04 <sup>4</sup> 1)	(13) 04401 (04 <sup>4</sup> 0)	2299.21	370.2
1	FrH	(48) 20012 (12 <sup>0</sup> 1)	(12) 20002 (12 <sup>0</sup> 0)	2306.70	379.5
1	FrH	(49) 12211 (12 <sup>2</sup> 1)	(14) 12201 (12 <sup>2</sup> 0)	2301.06	378.4
1	FrH	(50) 20011 (20 <sup>0</sup> 1)	(15) 20001 (20 <sup>0</sup> 0)	2302.52	380.0
1	FH $v_3$ ,FH	(51) 01121 (01 <sup>1</sup> 2)	(16) 01111 (01 <sup>1</sup> 1)	2311.70	806.5
1	5thH	(54) 21113 (05 <sup>1</sup> 1)	(17) 21103 (05 <sup>1</sup> 0)	2293.61	364.5
1	5thH	(56) 13312 (05 <sup>3</sup> 1)	(18) 13302 (05 <sup>3</sup> 0)	2290.68	368.4
1	5thH	(57) 05511 (05 <sup>5</sup> 1)	(20) 05501 (05 <sup>5</sup> 0)	2286.80	352.8
1	5thH	(58) 21112 (13 <sup>1</sup> 1)	(19) 21102 (13 <sup>1</sup> 0)	2293.41	370.7
1	5thH	(59) 13311 (13 <sup>3</sup> 1)	(21) 13301 (13 <sup>3</sup> 0)	2288.39	364.5
1	5thH	(60) 21111 (21 <sup>1</sup> 1)	(22) 21101 (21 <sup>1</sup> 0)	2289.90	369.5
1	FH $v_3$ ,SH	(61) 10022 (02 <sup>0</sup> 2)	(23) 10012 (02 <sup>0</sup> 1)	2302.37	787.4
1	FH $v_3$ ,SH	(62) 02221 (02 <sup>2</sup> 2)	(24) 02211 (02 <sup>2</sup> 1)	2299.24	781.8
1	FH $v_3$ ,SH	(63) 10021 (10 <sup>0</sup> 2)	(25) 10011 (10 <sup>0</sup> 1)	2301.91	782.2
1	6thH	(64) 30014 (06 <sup>0</sup> 1)	(26) 30004 (06 <sup>0</sup> 0)	2283.30	367.9

Continued on next page

Table A.1 continued

Iso <sup>◇</sup>	Band	Upper level <sup>†</sup>	Lower level <sup>†</sup>	$\tilde{\nu}_0^*$ (cm <sup>-1</sup> )	$A^\ddagger$ (s <sup>-1</sup> )
1	6thH	(65) 22213 (06 <sup>2</sup> 1)	(27) 22203 (06 <sup>2</sup> 0)	2281.67	364.5
1	6thH	(66) 14412 (06 <sup>4</sup> 1)	(28) 14402 (06 <sup>4</sup> 0)	2278.39	353.2
1	6thH	(68) 30013 (14 <sup>0</sup> 1)	(29) 30003 (14 <sup>0</sup> 0)	2285.37	360.5
1	6thH	(69) 06611 (06 <sup>6</sup> 1)	(31) 06601 (06 <sup>6</sup> 0)	2274.42	333.4
1	6thH	(70) 22212 (14 <sup>2</sup> 1)	(30) 22202 (14 <sup>2</sup> 0)	2280.62	359.7
1	6thH	(71) 30012 (22 <sup>0</sup> 1)	(32) 30002 (22 <sup>0</sup> 0)	2283.58	358.7
1	6thH	(73) 14411 (14 <sup>4</sup> 1)	(33) 14401 (14 <sup>4</sup> 0)	2275.84	349.1
1	6thH	(74) 22211 (22 <sup>2</sup> 1)	(34) 22201 (22 <sup>2</sup> 0)	2277.17	357.4
1	6thH	(75) 30011 (30 <sup>0</sup> 1)	(35) 30001 (30 <sup>0</sup> 0)	2277.98	359.8
1	FH $v_3$ ,TH	(76) 11122 (03 <sup>1</sup> 2)	(36) 11112 (03 <sup>1</sup> 1)	2290.25	768.4
1	FH $v_3$ ,TH	(77) 03321 (03 <sup>3</sup> 2)	(37) 03311 (03 <sup>3</sup> 1)	2286.80	753.6
1	FH $v_3$ ,TH	(78) 11121 (11 <sup>1</sup> 2)	(38) 11111 (11 <sup>1</sup> 1)	2289.08	762.0
1	SH $v_3$	(79) 00031 (00 <sup>0</sup> 3)	(39) 00021 (00 <sup>0</sup> 2)	2299.26	1211.0
1	SH $v_3$ ,FH	(93) 01131 (01 <sup>1</sup> 3)	(51) 01121 (01 <sup>1</sup> 2)	2286.80	1177.0
2	FB	(9) 00011 (00 <sup>0</sup> 1)	(1) 00001 (00 <sup>0</sup> 0)	2283.49	376.6
2	FH	(16) 01111 (01 <sup>1</sup> 1)	(2) 01101 (01 <sup>1</sup> 0)	2271.76	367.4
2	SH	(23) 10012 (02 <sup>0</sup> 1)	(3) 10002 (02 <sup>0</sup> 0)	2261.91	359.6
2	SH	(24) 02211 (02 <sup>2</sup> 1)	(4) 02201 (02 <sup>2</sup> 0)	2260.05	356.4
2	SH	(25) 10011 (10 <sup>0</sup> 1)	(5) 10001 (10 <sup>0</sup> 0)	2262.85	355.5
2	TH	(36) 11112 (03 <sup>1</sup> 1)	(6) 11102 (03 <sup>1</sup> 0)	2250.69	330.2
2	TH	(37) 03311 (03 <sup>3</sup> 1)	(7) 03301 (03 <sup>3</sup> 0)	2248.36	343.8
2	TH	(38) 11111 (11 <sup>1</sup> 1)	(8) 11101 (11 <sup>1</sup> 0)	2250.60	346.7
2	FH $v_3$	(39) 00021 (00 <sup>0</sup> 2)	(9) 00011 (00 <sup>0</sup> 1)	2260.06	735.7
2	FrH	(43) 20013 (04 <sup>0</sup> 1)	(10) 20003 (04 <sup>0</sup> 0)	2240.54	344.1
2	FrH	(44) 12212 (04 <sup>2</sup> 1)	(11) 12202 (04 <sup>2</sup> 0)	2239.30	340.5
2	FrH	(47) 04411 (04 <sup>4</sup> 1)	(13) 04401 (04 <sup>4</sup> 0)	2236.68	329.8
2	FrH	(48) 20012 (12 <sup>0</sup> 1)	(12) 20002 (12 <sup>0</sup> 0)	2242.32	337.6
2	FrH	(49) 12211 (12 <sup>2</sup> 1)	(14) 12201 (12 <sup>2</sup> 0)	2238.57	336.1
2	FrH	(50) 20011 (20 <sup>0</sup> 1)	(15) 20001 (20 <sup>0</sup> 0)	2240.76	336.0
3	FB	(9) 00011 (00 <sup>0</sup> 1)	(1) 00001 (00 <sup>0</sup> 0)	2332.11	418.7
3	FH	(16) 01111 (01 <sup>1</sup> 1)	(2) 01101 (01 <sup>1</sup> 0)	2319.74	408.8
3	SH	(23) 10012 (02 <sup>0</sup> 1)	(3) 10002 (02 <sup>0</sup> 0)	2311.71	398.0
3	SH	(24) 02211 (02 <sup>2</sup> 1)	(4) 02201 (02 <sup>2</sup> 0)	2307.38	795.2
3	SH	(25) 10011 (10 <sup>0</sup> 1)	(5) 10001 (10 <sup>0</sup> 0)	2309.29	397.6
4	FB	(9) 00011 (00 <sup>0</sup> 1)	(1) 00001 (00 <sup>0</sup> 0)	2340.01	409.1
4	FH	(16) 01111 (01 <sup>1</sup> 1)	(2) 01101 (01 <sup>1</sup> 0)	2327.58	399.0
4	SH	(23) 10012 (02 <sup>0</sup> 1)	(3) 10002 (02 <sup>0</sup> 0)	2318.96	388.8
4	SH	(25) 10011 (10 <sup>0</sup> 1)	(5) 10001 (10 <sup>0</sup> 0)	2317.32	387.5
5	FB	(9) 00011 (00 <sup>0</sup> 1)	(1) 00001 (00 <sup>0</sup> 0)	2265.97	369.4
6	FB	(9) 00011 (00 <sup>0</sup> 1)	(1) 00001 (00 <sup>0</sup> 0)	2274.09	380.6

Continued on next page

Table A.1 continued

Iso <sup>◇</sup> Band	Upper level <sup>†</sup>	Lower level <sup>†</sup>	$\tilde{\nu}_0^*$ (cm <sup>-1</sup> )	$A^\ddagger$ (s <sup>-1</sup> )
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◇The isotopologue numbers refer to those in the HITRAN compilation. †Energy levels are given with the HITRAN identifier number (in parenthesis) and the HITRAN and Herzberg (in parenthesis) notations. \*Band center. ‡Einstein coefficient at 250 K calculated from the HITRAN 2008 edition (Rothman et al., 2009). FB stands for fundamental band, FH for first hot ( $v_d=1$ ), SH for second hot ( $v_d=2$ ), TH for third hot ( $v_d=3$ ), FrH for fourth hot ( $v_d=4$ ), 5thH for fifth hot ( $v_d=5$ ), 6thH for sixth hot ( $v_d=6$ ), FH $v_3$  for  $v_3$ -first hot ( $v_3=2$ ), FH $v_3$ ,FH for  $v_3$ -first hot  $v_d$ -first hot ( $v_3=2, v_d=1$ ), FH $v_3$ ,SH for  $v_3$ -first hot  $v_d$ -second hot ( $v_3=2, v_d=2$ ), FH $v_3$ ,TH for  $v_3$ -first hot  $v_d$ -third hot ( $v_3=2, v_d=3$ ), SH $v_3$  for  $v_3$ -second hot ( $v_3 = 3$ ), and SH $v_3$ ,FH for  $v_3$ -second hot  $v_d$ -first hot ( $v_3=3, v_d=1$ ).



## Appendix B

# Table of CO<sub>2</sub> Sub-Microwindows

Table B.1: Sub-microwindows used in the joint retrieval of CO<sub>2</sub> and LOS.

Tangent Height (km)	Sub-microwindows (cm <sup>-1</sup> )			
60	2311.188-2311.250, 2319.812-2320.000, 2324.750-2324.938, 2328.562-2328.625, 2334.000-2334.062, 2353.000-2353.062,	2314.812-2314.938, 2320.562-2320.688, 2326.188-2326.250, 2329.250-2329.312, 2339.438-2339.500, 2354.375-2354.500,	2317.062-2317.375, 2321.438-2321.625, 2326.625-2326.812, 2330.000-2330.062, 2340.938-2341.000, 2355.938-2356.125,	2319.000-2319.188, 2323.000-2323.250, 2326.938-2327.062, 2332.500-2332.562, 2346.062-2346.125, 2360.188-2360.312
63	2309.625-2309.688, 2314.688-2314.938, 2317.438-2317.500, 2321.188-2321.688, 2326.000-2326.250, 2329.250-2329.312, 2334.000-2334.062, 2342.625-2342.688, 2355.750-2356.062, 2365.250-2365.500	2310.375-2310.500, 2315.250-2315.312, 2318.875-2319.188, 2322.812-2323.250, 2326.625-2327.062, 2330.562-2330.750, 2337.688-2337.750, 2344.312-2344.500, 2358.562-2358.875,	2311.125-2311.438, 2316.188-2316.250, 2319.688-2320.000, 2324.688-2324.938, 2328.562-2328.625, 2332.125-2332.250, 2339.312-2339.562, 2345.875-2346.125, 2361.312-2361.625,	2313.625-2313.812, 2317.062-2317.312, 2320.312-2320.688, 2325.375-2325.625, 2329.000-2329.062, 2332.500-2332.562, 2340.875-2341.000, 2354.375-2354.562, 2363.938-2364.250,
66	2310.438-2310.562, 2318.938-2319.188, 2321.438-2321.688, 2326.188-2326.250, 2330.562-2330.625, 2339.312-2339.500, 2345.938-2346.125, 2358.562-2358.875, 2364.000-2364.250,	2311.125-2311.250, 2319.750-2320.000, 2323.000-2323.312, 2326.625-2327.062, 2332.438-2332.562, 2340.938-2341.000, 2354.312-2354.500, 2360.000-2360.250, 2365.250-2365.500	2314.812-2314.938, 2320.312-2320.375, 2324.750-2324.938, 2328.562-2328.625, 2334.000-2334.062, 2342.625-2342.688, 2355.812-2356.062, 2361.312-2361.562,	2315.250-2315.312, 2320.562-2320.688, 2325.562-2325.625, 2328.750-2328.812, 2335.938-2336.000, 2344.312-2344.375, 2357.188-2357.438, 2362.750-2362.938,

Continued on next page

Table B.1 continued

Tangent Height (km)	Sub-microwindows (cm <sup>-1</sup> )			
69	2310.438-2310.562, 2320.562-2320.688, 2326.688-2327.062, 2335.938-2336.000, 2344.312-2344.375, 2358.625-2358.750,	2314.812-2314.938, 2321.125-2321.188, 2328.562-2328.812, 2339.312-2339.500, 2354.312-2354.500, 2362.750-2362.938	2318.938-2319.188, 2324.750-2324.938, 2332.438-2332.500, 2340.938-2341.000, 2355.875-2356.000,	2319.750-2319.938, 2326.188-2326.250, 2334.000-2334.062, 2342.625-2342.688, 2357.188-2357.438,
72	2323.250-2323.312, 2334.000-2334.062, 2346.625-2346.688, 2352.125-2352.250	2323.875-2324.188, 2335.938-2336.062, 2347.562-2347.625,	2324.875-2324.938, 2340.938-2341.000, 2349.938-2350.000,	2328.625-2328.812, 2342.625-2342.688, 2350.938-2351.125,
75	2307.188-2307.250, 2309.625-2309.688, 2321.125-2321.188, 2323.875-2324.188, 2336.312-2336.438, 2342.250-2342.312, 2347.562-2347.812,	2308.125-2308.188, 2316.125-2316.188, 2321.625-2321.688, 2328.750-2328.812, 2336.625-2336.688, 2342.625-2342.688, 2349.750-2350.062,	2308.312-2308.375, 2317.500-2317.562, 2321.938-2322.000, 2329.000-2329.062, 2337.688-2337.750, 2344.188-2344.250, 2350.875-2351.125	2309.000-2309.062, 2320.312-2320.375, 2323.562-2323.625, 2335.875-2336.062, 2340.938-2341.000, 2346.562-2346.688,
78	2306.000-2306.312, 2308.750-2309.062, 2311.688-2311.750, 2313.438-2313.625, 2317.500-2317.562, 2320.000-2320.062, 2321.688-2321.750, 2323.938-2324.188, 2331.125-2331.375, 2335.750-2336.062, 2339.625-2339.688, 2342.688-2342.938,	2306.938-2307.188, 2309.625-2309.688, 2312.312-2312.375, 2314.312-2314.438, 2317.750-2317.875, 2320.312-2320.375, 2321.938-2322.000, 2329.625-2329.875, 2332.000-2332.062, 2336.875-2336.938, 2339.875-2339.938, 2343.938-2344.188,	2307.812-2307.875, 2310.562-2310.625, 2312.562-2312.625, 2316.062-2316.188, 2318.625-2318.688, 2320.875-2320.938, 2322.500-2322.812, 2330.250-2330.312, 2332.812-2332.875, 2337.125-2337.188, 2340.938-2341.250, 2344.875-2345.438,	2308.000-2308.125, 2311.438-2311.500, 2313.188-2313.250, 2316.938-2317.000, 2319.188-2319.312, 2321.125-2321.188, 2323.312-2323.562, 2330.500-2330.562, 2334.062-2334.125, 2338.500-2338.625, 2342.312-2342.438, 2346.125-2346.625
81	2306.000-2306.312, 2309.625-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.375, 2323.312-2323.562, 2332.562-2332.875, 2335.500-2335.812, 2338.312-2338.625, 2341.000-2341.250, 2343.938-2344.188,	2306.938-2307.188, 2310.562-2310.812, 2314.062-2314.438, 2317.500-2317.875, 2320.875-2321.188, 2330.250-2330.562, 2333.188-2333.500, 2336.000-2336.312, 2338.812-2339.062, 2341.438-2341.688, 2344.875-2345.125	2307.875-2308.125, 2311.438-2311.750, 2314.938-2315.250, 2318.375-2318.688, 2321.688-2322.000, 2331.125-2331.375, 2334.062-2334.375, 2336.875-2337.188, 2339.625-2339.938, 2342.312-2342.562,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.188-2319.500, 2322.500-2322.812, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.688, 2340.062-2340.375, 2342.688-2342.938,

Continued on next page

Table B.1 continued

Tangent Height (km)	Sub-microwindows ( $\text{cm}^{-1}$ )			
84	2306.062-2306.312, 2309.625-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.312, 2323.312-2323.562, 2332.562-2332.812, 2335.500-2335.688, 2338.312-2338.625, 2341.000-2341.250, 2343.938-2344.188	2306.938-2307.188, 2310.562-2310.812, 2314.062-2314.438, 2317.562-2317.812, 2320.875-2321.188, 2330.250-2330.562, 2333.188-2333.500, 2336.000-2336.312, 2338.812-2339.000, 2341.438-2341.688,	2307.875-2308.062, 2311.500-2311.750, 2314.938-2315.250, 2318.438-2318.688, 2321.688-2321.938, 2331.125-2331.312, 2334.062-2334.250, 2336.938-2337.188, 2339.625-2339.938, 2342.312-2342.562,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.188-2319.500, 2322.500-2322.750, 2331.750-2332.000, 2334.688-2334.875, 2337.438-2337.688, 2340.062-2340.375, 2342.688-2342.938,
87	2306.000-2306.312, 2309.688-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.312, 2323.312-2323.562, 2332.562-2332.875, 2335.500-2335.812, 2338.312-2338.625, 2341.000-2341.250, 2343.938-2344.188	2306.938-2307.188, 2310.562-2310.812, 2314.062-2314.375, 2317.500-2317.812, 2320.875-2321.188, 2330.250-2330.562, 2333.188-2333.500, 2336.000-2336.312, 2338.812-2339.062, 2341.438-2341.688,	2307.875-2308.125, 2311.438-2311.750, 2314.938-2315.250, 2318.375-2318.688, 2321.688-2322.000, 2331.125-2331.375, 2334.062-2334.375, 2336.875-2337.188, 2339.625-2339.938, 2342.312-2342.562,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.188-2319.500, 2322.500-2322.812, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.688, 2340.062-2340.375, 2342.688-2342.938,
90	2306.000-2306.312, 2309.688-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.312, 2323.312-2323.562, 2332.562-2332.875, 2335.500-2335.812, 2338.312-2338.625, 2341.000-2341.250, 2343.938-2344.188	2306.938-2307.188, 2310.562-2310.812, 2314.062-2314.375, 2317.500-2317.812, 2320.875-2321.188, 2330.250-2330.562, 2333.188-2333.500, 2336.000-2336.312, 2338.812-2339.062, 2341.438-2341.688,	2307.875-2308.125, 2311.438-2311.750, 2314.938-2315.250, 2318.375-2318.688, 2321.688-2322.000, 2331.125-2331.375, 2334.062-2334.375, 2336.875-2337.188, 2339.625-2339.938, 2342.312-2342.562,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.188-2319.500, 2322.500-2322.812, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.688, 2340.062-2340.375, 2342.688-2342.938,
93	2306.000-2306.312, 2309.688-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.312, 2323.312-2323.562, 2332.562-2332.875, 2335.500-2335.812, 2338.312-2338.562, 2341.062-2341.312, 2343.938-2344.188	2306.938-2307.188, 2310.562-2310.812, 2314.125-2314.375, 2317.500-2317.812, 2320.875-2321.125, 2330.250-2330.500, 2333.188-2333.500, 2336.062-2336.312, 2338.812-2339.062, 2341.438-2341.688,	2307.875-2308.125, 2311.438-2311.750, 2314.938-2315.250, 2318.375-2318.688, 2321.688-2322.000, 2331.125-2331.375, 2334.125-2334.375, 2336.875-2337.188, 2339.625-2339.938, 2342.312-2342.562,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.250-2319.500, 2322.500-2322.812, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.625, 2340.062-2340.375, 2342.688-2342.938,

Continued on next page

Table B.1 continued

Tangent Height (km)	Sub-microwindows (cm <sup>-1</sup> )			
96	2306.000-2306.312, 2309.688-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.312, 2323.312-2323.562, 2333.188-2333.500, 2336.062-2336.312, 2338.812-2339.062, 2341.438-2341.688, 2346.125-2346.375	2306.938-2307.188, 2310.562-2310.812, 2314.125-2314.375, 2317.500-2317.812, 2320.875-2321.062, 2330.250-2330.500, 2334.125-2334.375, 2336.875-2337.188, 2339.625-2339.938, 2342.312-2342.562,	2307.875-2308.125, 2311.438-2311.750, 2314.938-2315.312, 2318.375-2318.688, 2321.688-2322.000, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.625, 2340.062-2340.375, 2342.688-2342.938,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.250-2319.500, 2322.562-2322.812, 2332.562-2332.875, 2335.500-2335.812, 2338.312-2338.562, 2341.062-2341.312, 2343.938-2344.188,
99	2306.000-2306.312, 2309.688-2309.938, 2313.188-2313.562, 2316.688-2317.000, 2320.000-2320.312, 2324.125-2324.375, 2333.250-2333.500, 2336.062-2336.312, 2338.812-2339.062, 2341.438-2341.688, 2347.500-2347.750	2306.938-2307.188, 2310.562-2310.812, 2314.125-2314.375, 2317.500-2317.812, 2320.875-2321.062, 2330.250-2330.438, 2334.125-2334.375, 2336.875-2337.188, 2339.625-2339.938, 2342.312-2342.938,	2307.875-2308.125, 2311.438-2311.750, 2314.938-2315.312, 2318.375-2318.688, 2321.688-2322.000, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.625, 2340.062-2340.375, 2343.938-2344.250,	2308.750-2309.000, 2312.312-2312.625, 2315.875-2316.125, 2319.250-2319.500, 2323.250-2323.562, 2332.562-2332.875, 2335.500-2335.812, 2338.312-2338.562, 2341.062-2341.312, 2346.125-2346.375,
102	2306.000-2306.312, 2309.688-2309.938, 2312.375-2312.625, 2315.875-2316.125, 2319.250-2319.500, 2323.250-2323.562, 2330.312-2330.500, 2334.125-2334.375, 2336.938-2337.188, 2339.625-2339.938, 2342.312-2342.938, 2349.750-2350.062,	2307.000-2307.188, 2310.562-2310.812, 2313.062-2313.562, 2316.688-2317.312, 2320.062-2320.312, 2324.125-2324.438, 2331.750-2332.062, 2334.625-2334.938, 2337.438-2337.625, 2340.062-2340.375, 2343.625-2344.250, 2352.812-2353.062	2307.875-2308.125, 2310.938-2311.188, 2314.125-2314.375, 2317.562-2317.812, 2320.875-2321.250, 2325.000-2325.188, 2332.562-2332.875, 2335.500-2335.750, 2338.312-2338.562, 2341.062-2341.312, 2346.125-2346.375,	2308.875-2309.188, 2311.500-2311.750, 2315.000-2315.375, 2318.375-2318.688, 2321.688-2321.938, 2326.688-2327.000, 2333.250-2333.500, 2336.062-2336.312, 2338.812-2339.062, 2341.438-2341.688, 2347.438-2347.750,

Continued on next page



Table B.1 continued

Tangent Height (km)	Sub-microwindows ( $\text{cm}^{-1}$ )			
107	2306.812-2307.062, 2315.000-2315.375, 2322.938-2323.188, 2330.438-2330.688, 2337.500-2337.812, 2344.250-2344.500, 2351.312-2351.625, 2357.188-2357.438, 2365.250-2365.500, 2372.438-2372.688, 2376.750-2376.938	2308.875-2309.188, 2317.000-2317.312, 2324.812-2325.125, 2332.250-2332.500, 2339.250-2339.500, 2345.875-2346.125, 2352.812-2353.125, 2358.625-2358.875, 2367.750-2368.000, 2373.562-2373.750,	2310.938-2311.250, 2319.000-2319.312, 2326.688-2327.000, 2334.000-2334.312, 2340.938-2341.250, 2347.438-2347.750, 2354.312-2354.562, 2360.000-2360.250, 2370.188-2370.375, 2374.625-2374.875,	2313.062-2313.312, 2321.000-2321.312, 2328.562-2328.875, 2335.812-2336.062, 2342.562-2342.875, 2349.750-2350.062, 2355.750-2356.000, 2362.688-2362.875, 2371.312-2371.562, 2375.688-2375.938,
112	2306.812-2307.062, 2315.000-2315.375, 2322.938-2323.188, 2330.375-2330.688, 2337.500-2337.812, 2344.188-2344.500, 2351.312-2351.625, 2357.188-2357.438, 2362.688-2362.938, 2367.750-2368.000, 2372.438-2372.688, 2376.688-2376.938,	2308.875-2309.188, 2317.000-2317.312, 2324.812-2325.125, 2332.250-2332.500, 2339.250-2339.500, 2345.875-2346.125, 2352.812-2353.125, 2358.625-2358.875, 2364.000-2364.250, 2368.938-2369.188, 2373.562-2373.812, 2377.750-2377.938	2310.938-2311.250, 2319.000-2319.312, 2326.750-2327.000, 2334.062-2334.312, 2340.938-2341.250, 2347.438-2347.750, 2354.250-2354.625, 2359.938-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2313.062-2313.312, 2321.000-2321.312, 2328.562-2328.875, 2335.750-2336.062, 2342.562-2342.875, 2349.750-2350.062, 2355.750-2356.062, 2361.312-2361.625, 2366.562-2366.750, 2371.312-2371.562, 2375.688-2375.938,
117	2311.000-2311.250, 2319.000-2319.312, 2326.750-2327.000, 2334.062-2334.312, 2340.938-2341.250, 2347.438-2347.750, 2355.750-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938	2313.062-2313.312, 2321.000-2321.312, 2328.562-2328.875, 2335.750-2336.062, 2342.562-2342.875, 2351.312-2351.625, 2357.188-2357.438, 2362.688-2362.938, 2367.750-2368.062, 2372.438-2372.688,	2315.062-2315.312, 2322.938-2323.188, 2330.375-2330.688, 2337.500-2337.812, 2344.188-2344.500, 2352.812-2353.125, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.188, 2373.562-2373.812,	2317.062-2317.312, 2324.875-2325.125, 2332.250-2332.562, 2339.188-2339.500, 2345.875-2346.125, 2354.250-2354.625, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,
122	2313.062-2313.312, 2321.000-2321.250, 2328.562-2328.875, 2335.812-2336.062, 2342.562-2342.875, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2315.062-2315.312, 2322.938-2323.188, 2330.375-2330.688, 2337.500-2337.750, 2344.250-2344.500, 2355.750-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938	2317.062-2317.312, 2324.875-2325.125, 2332.250-2332.500, 2339.250-2339.500, 2345.875-2346.125, 2357.188-2357.438, 2362.688-2362.938, 2367.750-2368.062, 2372.438-2372.688,	2319.000-2319.312, 2326.750-2327.000, 2334.062-2334.312, 2340.938-2341.250, 2352.812-2353.125, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812,

Continued on next page

Table B.1 continued

Tangent Height (km)	Sub-microwindows (cm <sup>-1</sup> )			
127	2311.000-2311.188, 2319.000-2319.312, 2326.750-2327.000, 2334.062-2334.312, 2340.938-2341.250, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2313.062-2313.312, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2355.750-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938	2315.062-2315.312, 2322.938-2323.188, 2330.375-2330.688, 2337.500-2337.750, 2344.250-2344.500, 2357.188-2357.438, 2362.688-2362.938, 2367.750-2368.062, 2372.438-2372.688,	2317.062-2317.312, 2324.875-2325.125, 2332.250-2332.500, 2339.250-2339.500, 2352.812-2353.062, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812,
132	2311.000-2311.188, 2319.000-2319.250, 2326.688-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2313.062-2313.312, 2321.062-2321.312, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2355.750-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938	2315.062-2315.250, 2322.938-2323.125, 2330.438-2330.625, 2337.500-2337.750, 2344.250-2344.500, 2357.188-2357.438, 2362.688-2362.938, 2367.750-2368.062, 2372.438-2372.688,	2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.188-2339.500, 2352.812-2353.062, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812,
137	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.750-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938	2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812,	2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,
142	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,

Continued on next page

Table B.1 continued

Tangent Height (km)	Sub-microwindows ( $\text{cm}^{-1}$ )			
147	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,
152	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,
157	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,
162	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,

Continued on next page

Table B.1 continued

Tangent Height (km)	Sub-microwindows (cm <sup>-1</sup> )			
167	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,
172	2306.938-2307.000, 2315.062-2315.250, 2323.000-2323.125, 2330.438-2330.625, 2337.500-2337.812, 2344.250-2344.500, 2358.625-2358.875, 2363.938-2364.250, 2368.938-2369.250, 2373.562-2373.812, 2377.750-2377.938	2308.938-2309.125, 2317.062-2317.250, 2324.875-2325.062, 2332.250-2332.438, 2339.250-2339.500, 2354.312-2354.562, 2360.000-2360.250, 2365.250-2365.500, 2370.125-2370.375, 2374.625-2374.875,	2311.000-2311.125, 2319.000-2319.250, 2326.750-2327.000, 2334.000-2334.250, 2340.938-2341.188, 2355.812-2356.062, 2361.312-2361.562, 2366.500-2366.750, 2371.312-2371.562, 2375.688-2375.938,	2313.000-2313.250, 2321.062-2321.250, 2328.562-2328.812, 2335.812-2336.062, 2342.562-2342.875, 2357.188-2357.438, 2362.688-2362.938, 2367.688-2368.062, 2372.438-2372.688, 2376.688-2376.938,

## Appendix C

# Figures of the Comparison of MIPAS CO<sub>2</sub> with ACE, SABER, and WACCM

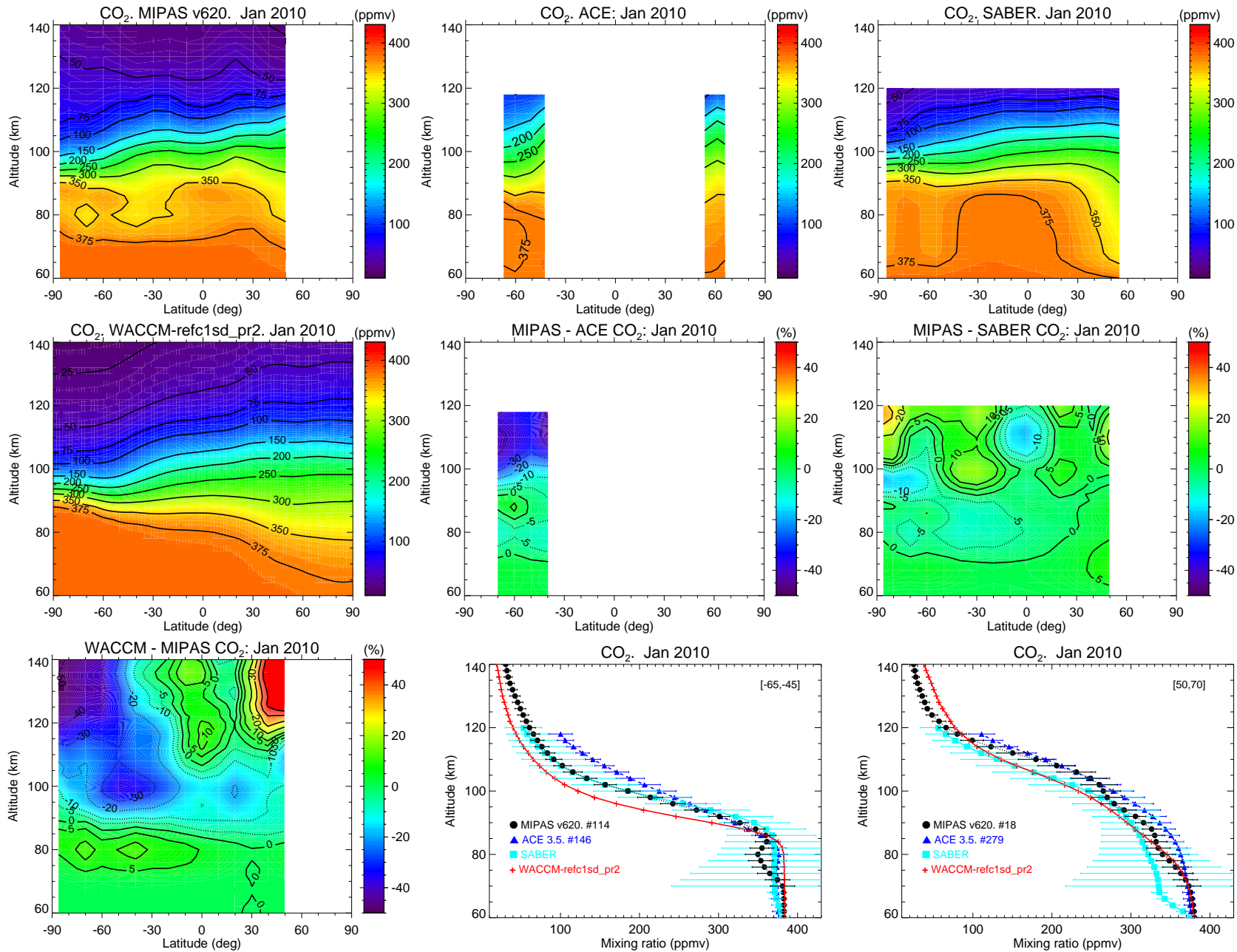


Figure C.1: CO<sub>2</sub> vmr abundances for January 2010. Top row: zonal mean distribution of MIPAS, ACE and SABER, respectively. Middle row: SD-WACCM ( $P_r=2$ ) CO<sub>2</sub> distribution, and MIPAS-ACE and MIPAS-SABER CO<sub>2</sub> relative differences in %. Bottom row: WACCM-MIPAS CO<sub>2</sub> differences, and CO<sub>2</sub> vmr profiles for two latitude bands (as labelled) corresponding roughly to the ACE measurements. Horizontal bars in the measurements are the total errors, dominated by the systematic errors.

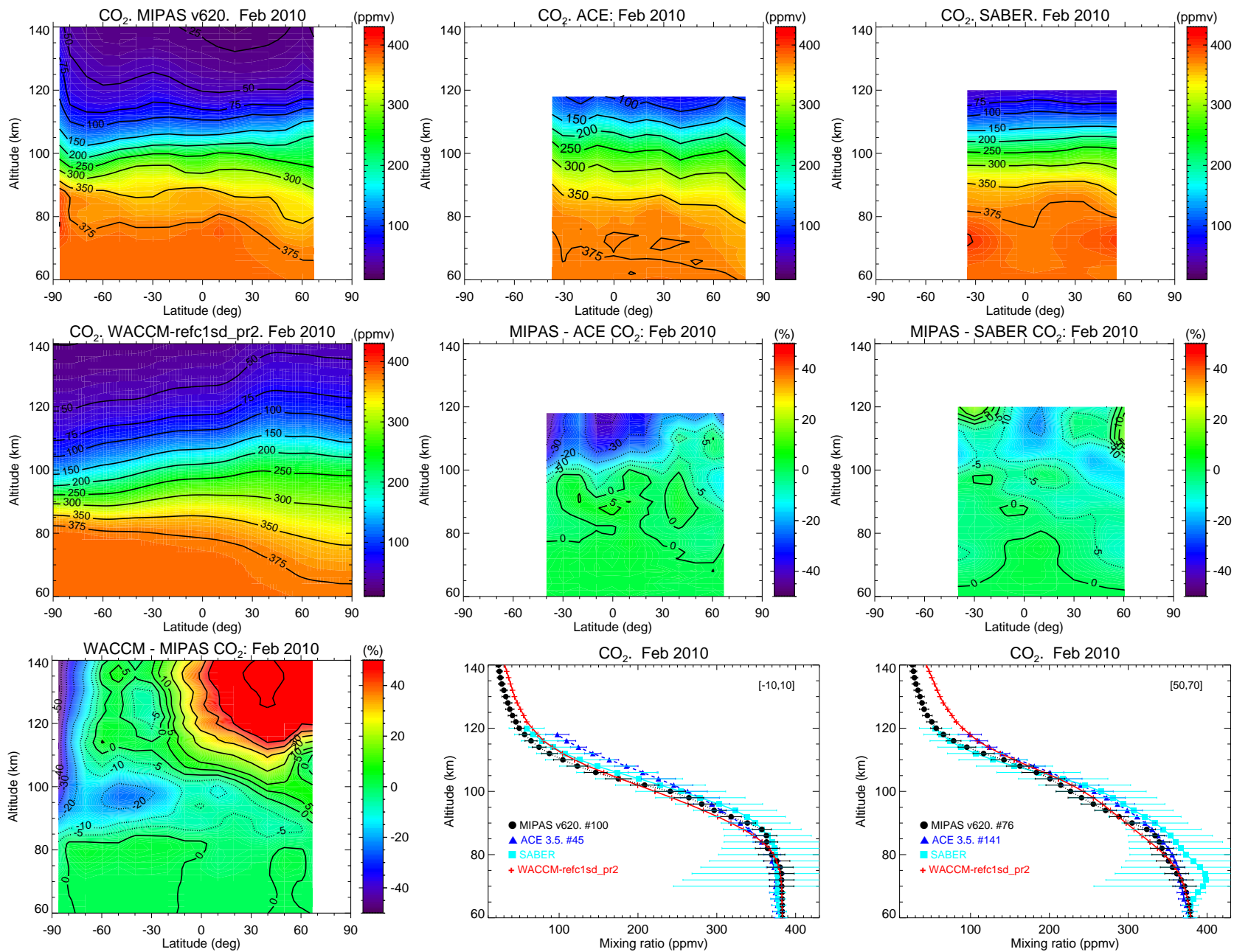


Figure C.2: As Fig. C.1 but for February 2010. Note that the latitude bands in the profiles panels can be different.



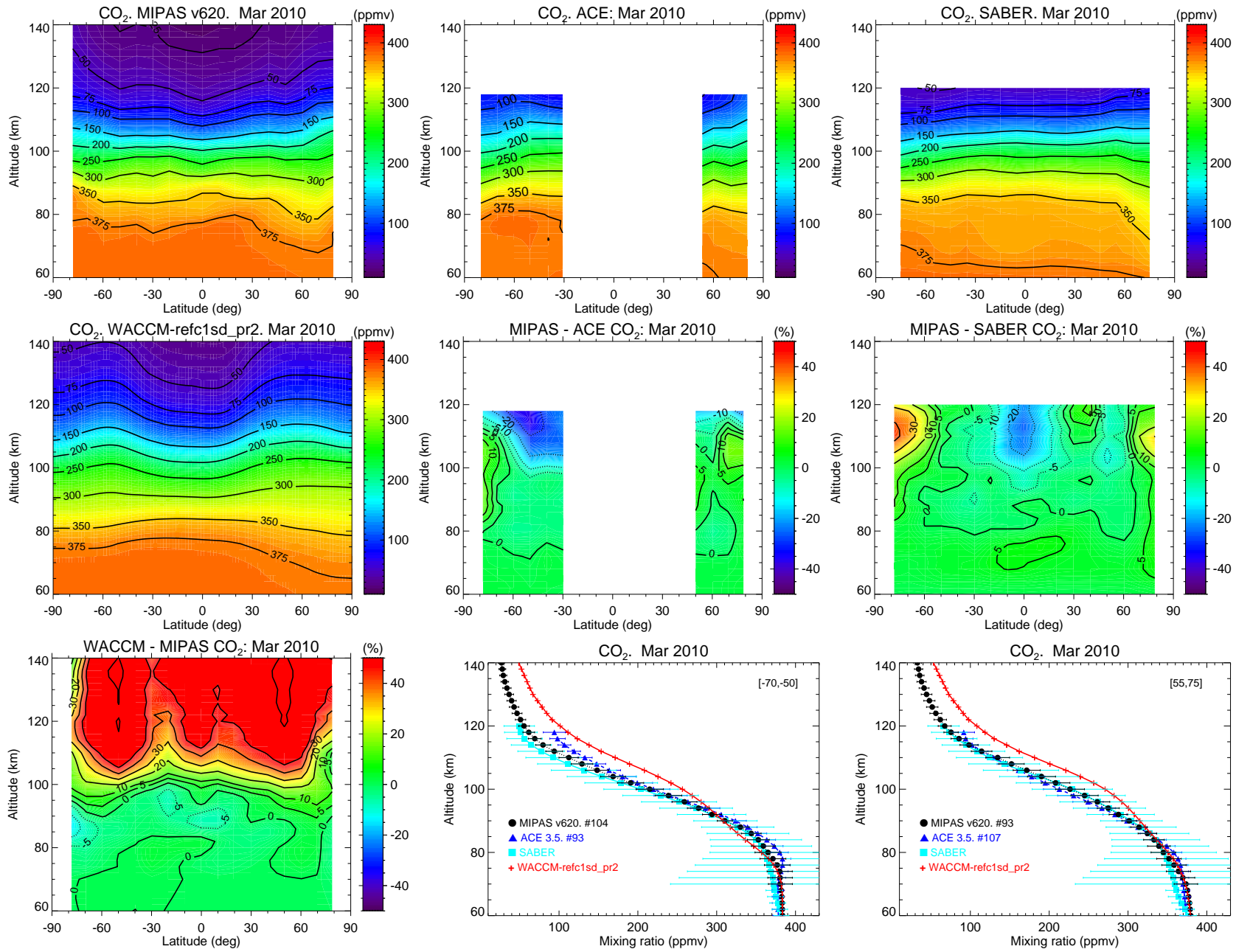


Figure C.3: As Fig. C.1 but for March 2010. Note that the latitude bands in the profiles panels can be different.



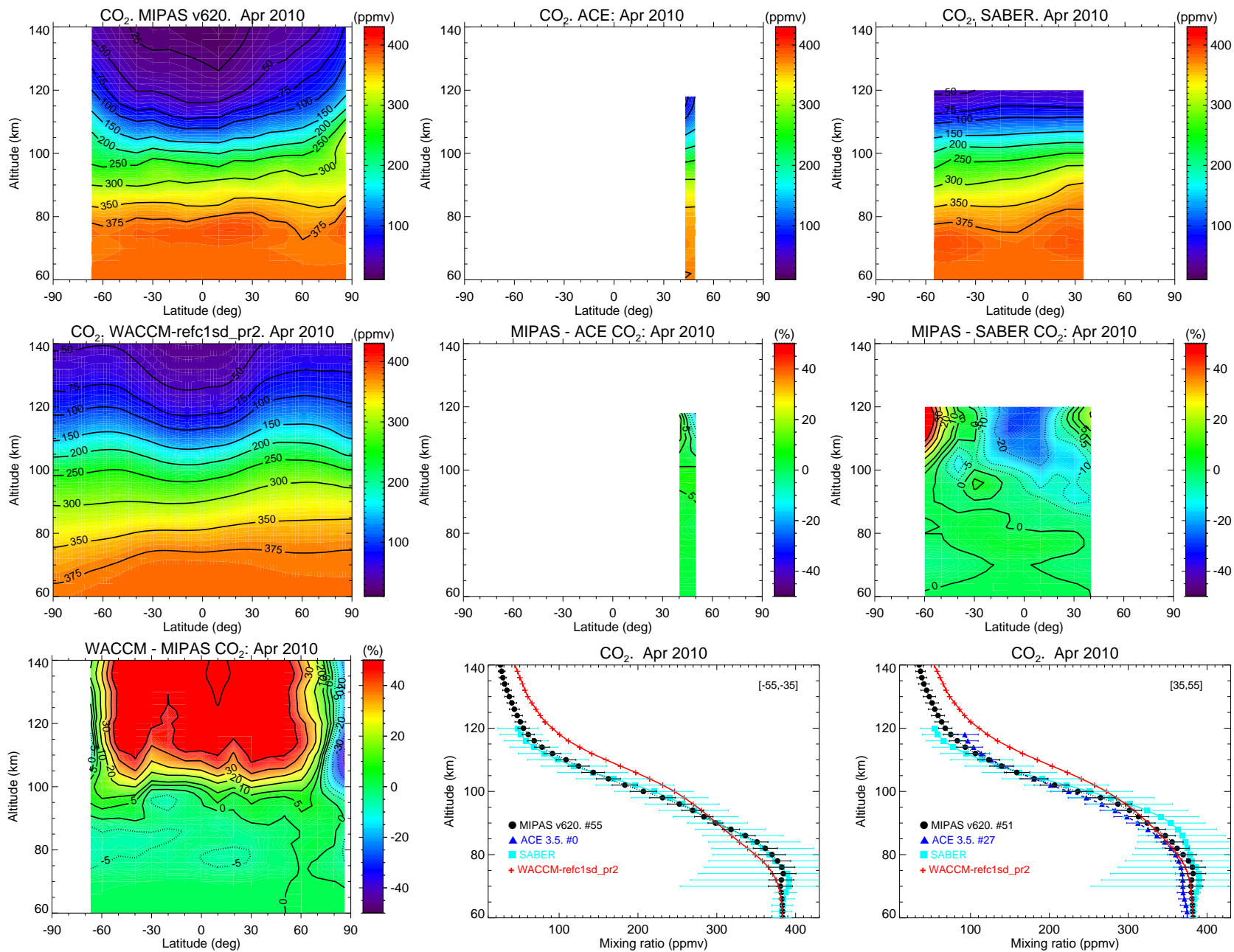


Figure C.4: As Fig. C.1 but for April 2010. Note that the latitude bands in the profiles panels can be different.

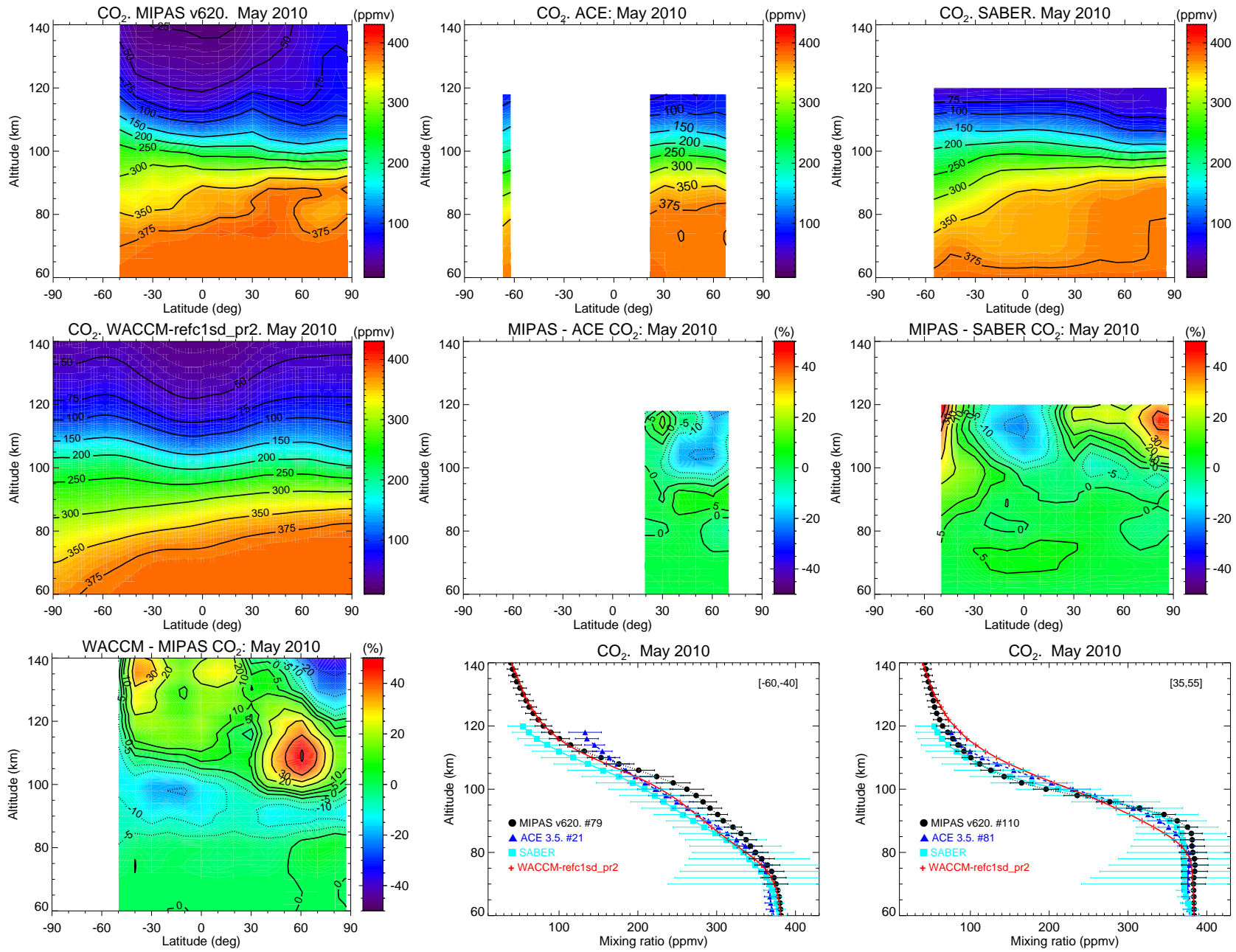


Figure C.5: As Fig. C.1 but for May 2010. Note that the latitude bands in the profiles panels can be different.

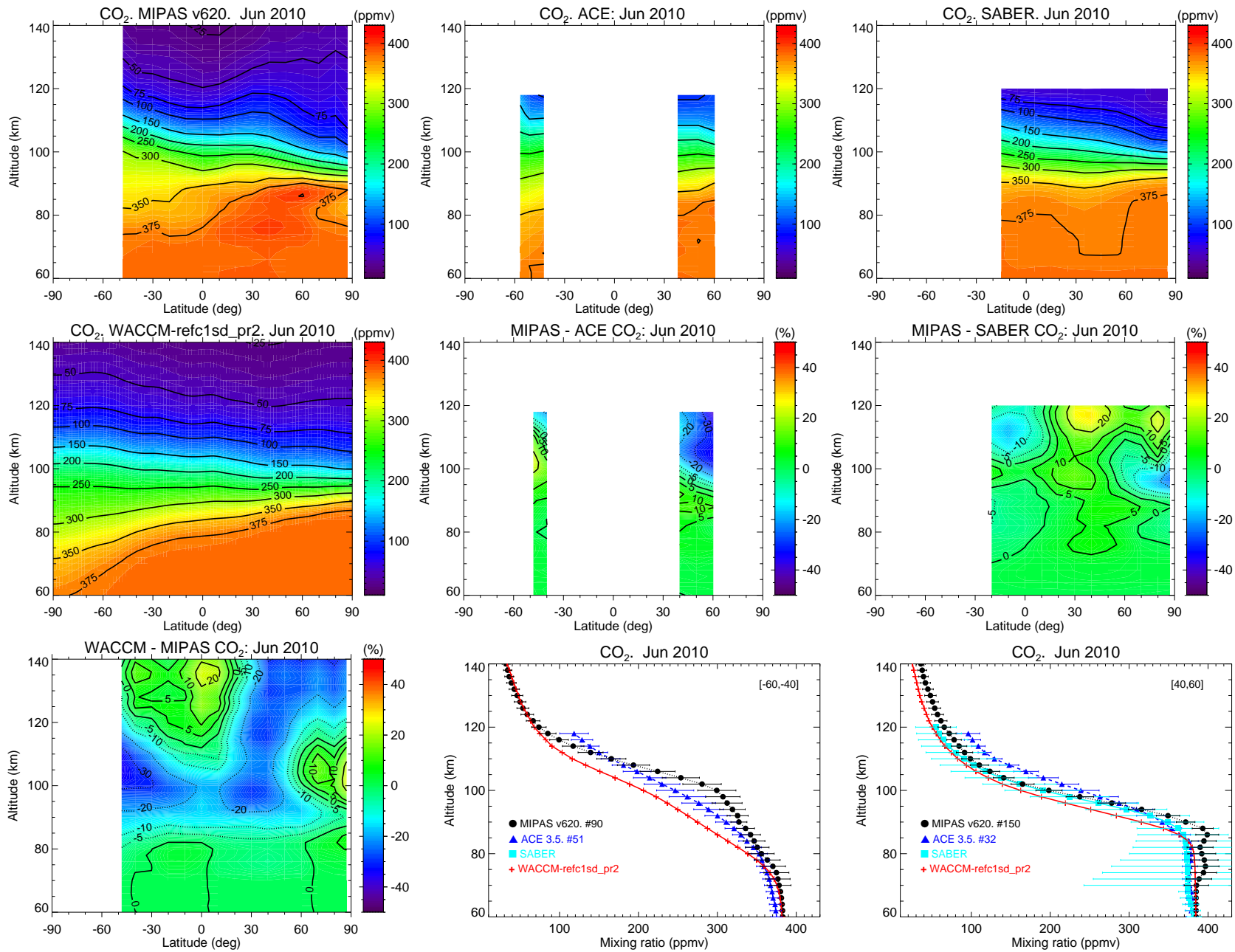


Figure C.6: As Fig. C.1 but for June 2010. Note that the latitude bands in the profiles panels can be different.

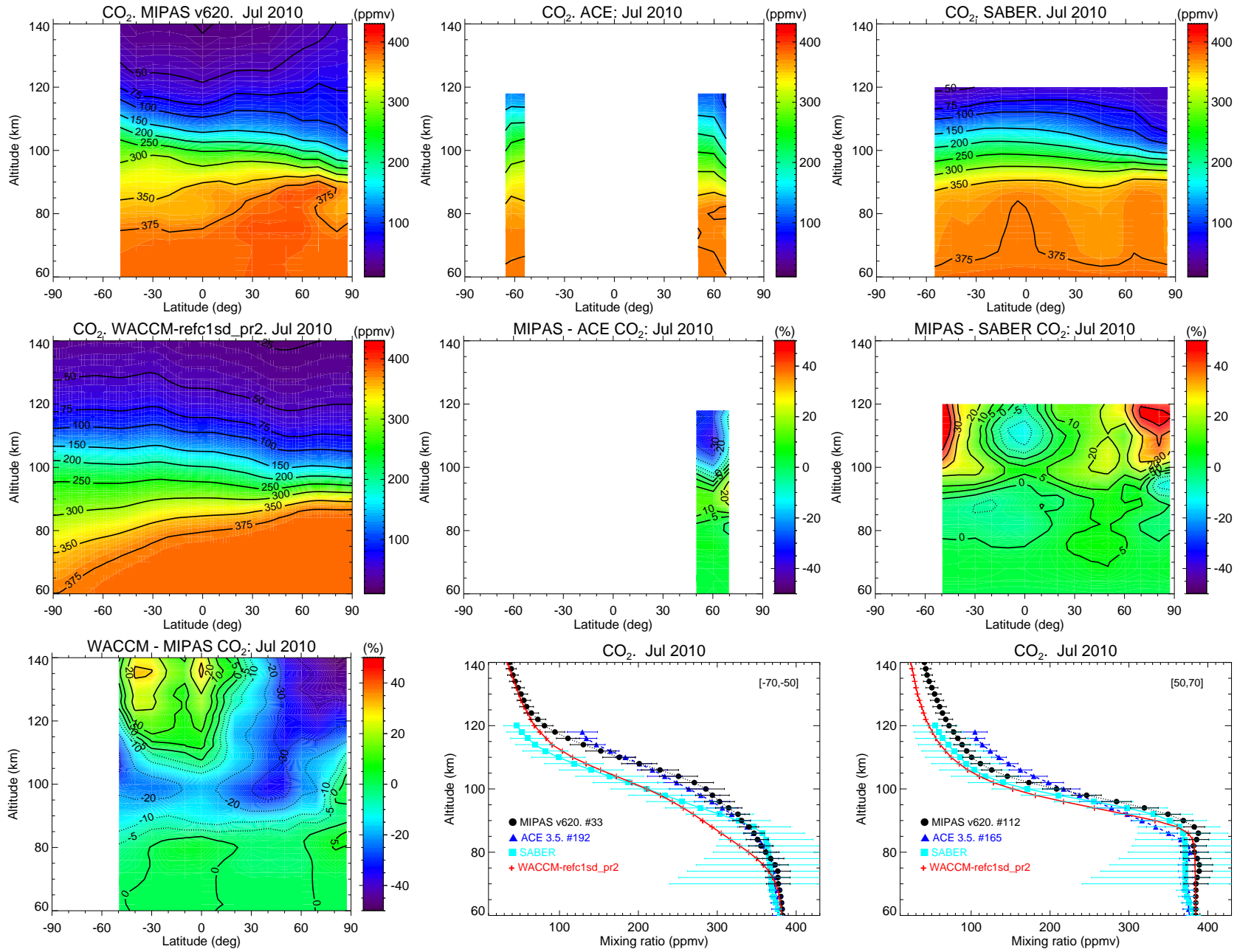


Figure C.7: As Fig. C.1 but for July 2010. Note that the latitude bands in the profiles panels can be different.



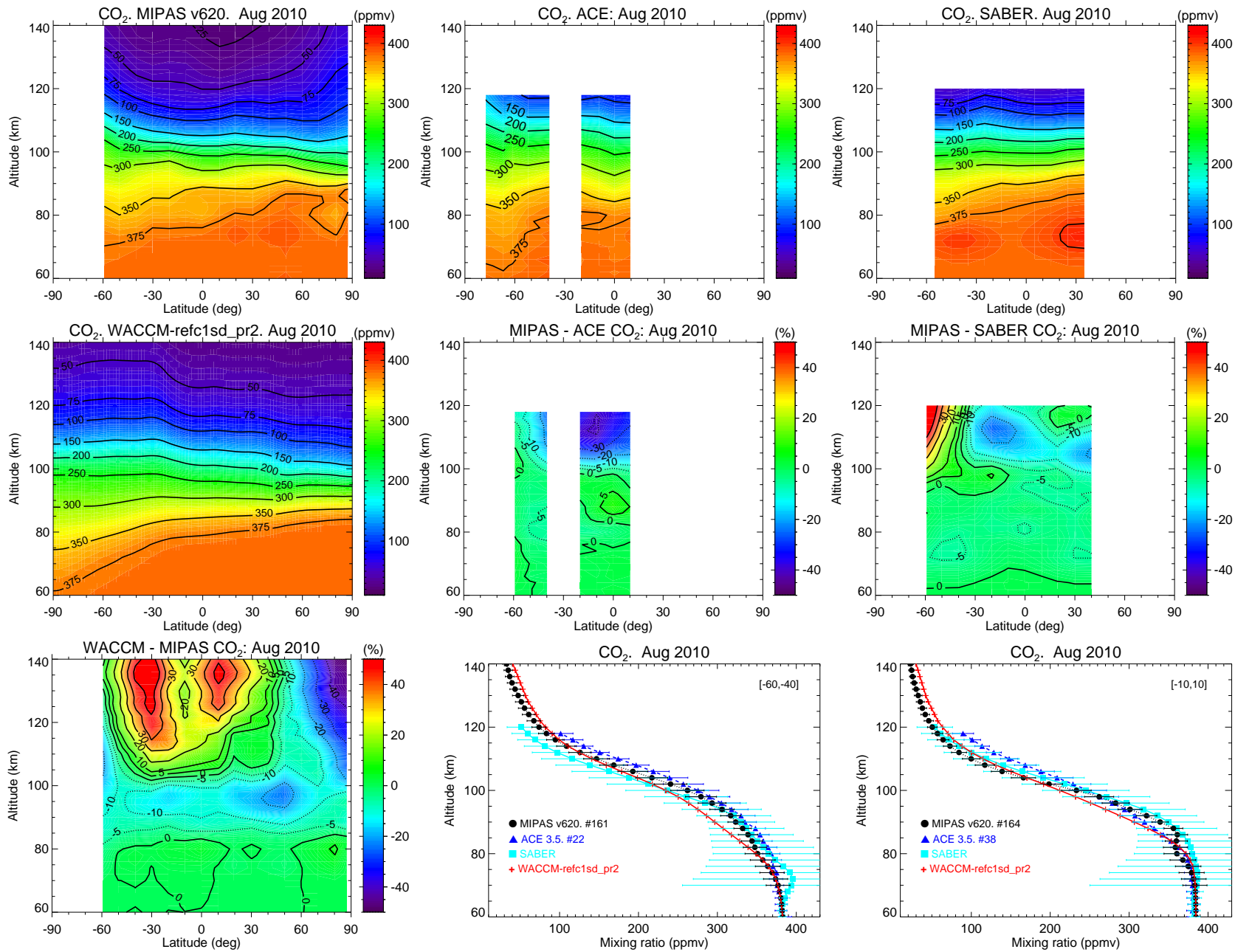


Figure C.8: As Fig. C.1 but for August 2010. Note that the latitude bands in the profiles panels can be different.

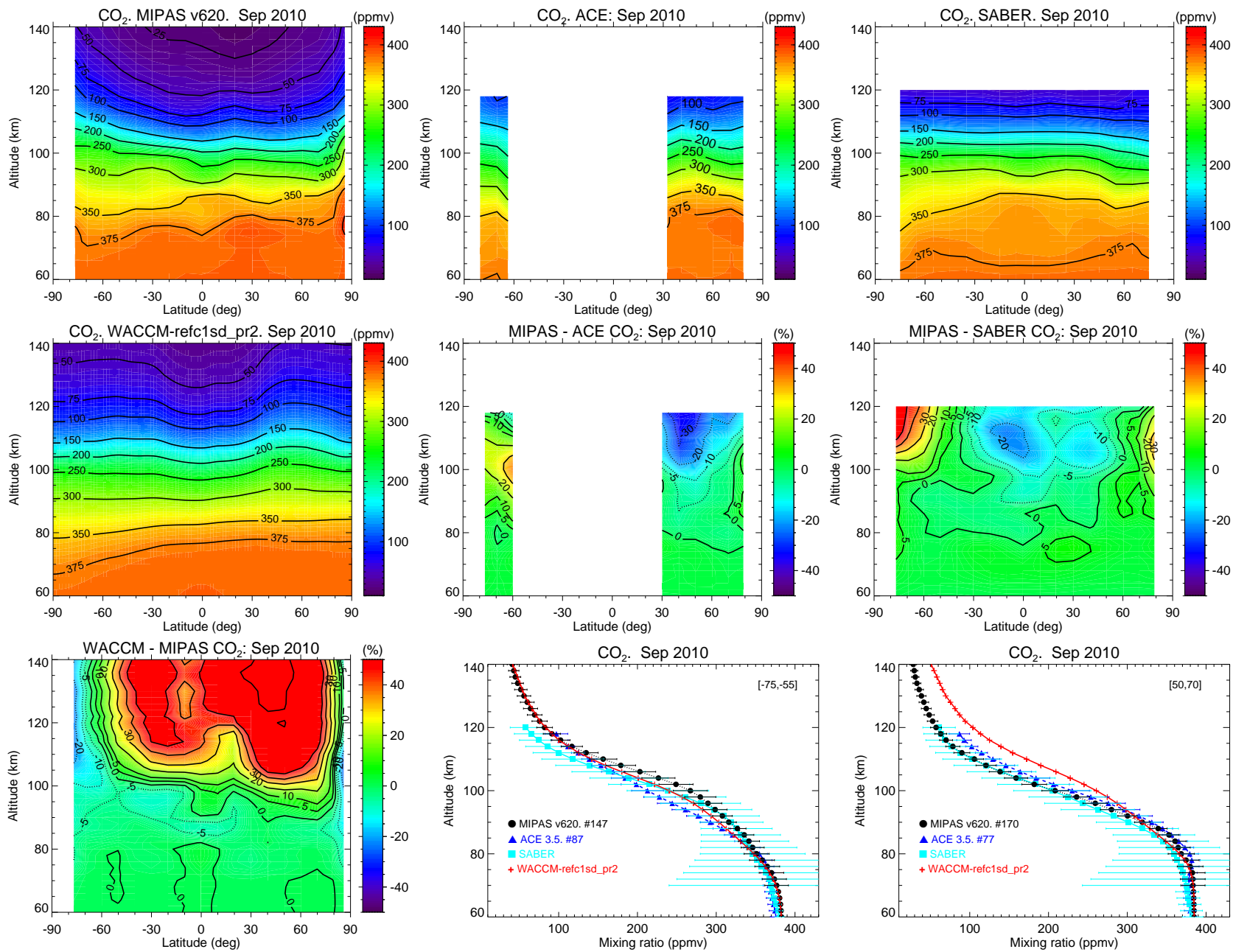


Figure C.9: As Fig. C.1 but for September 2010. Note that the latitude bands in the profiles panels can be different.

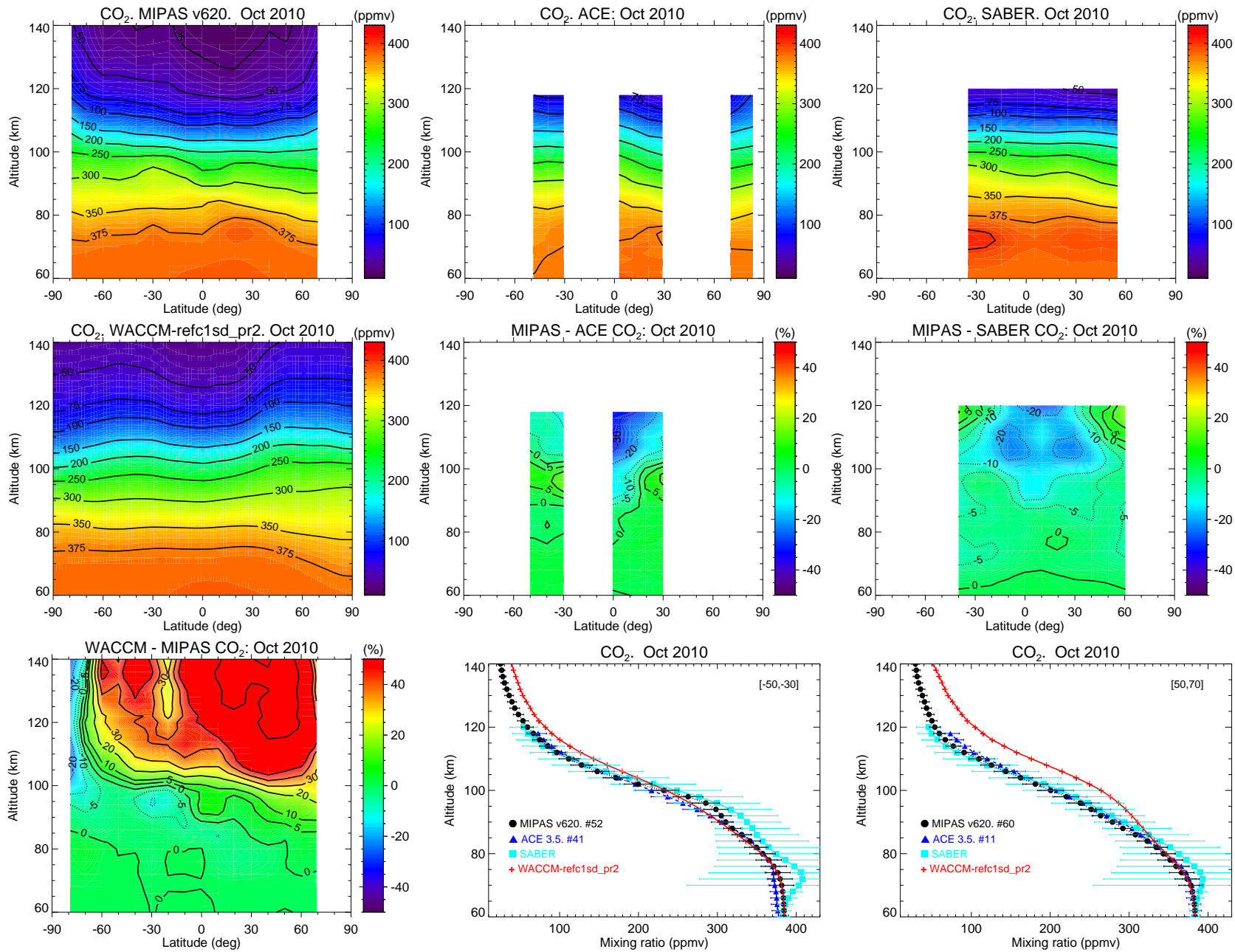


Figure C.10: As Fig. C.1 but for October 2010. Note that the latitude bands in the profiles panels can be different.

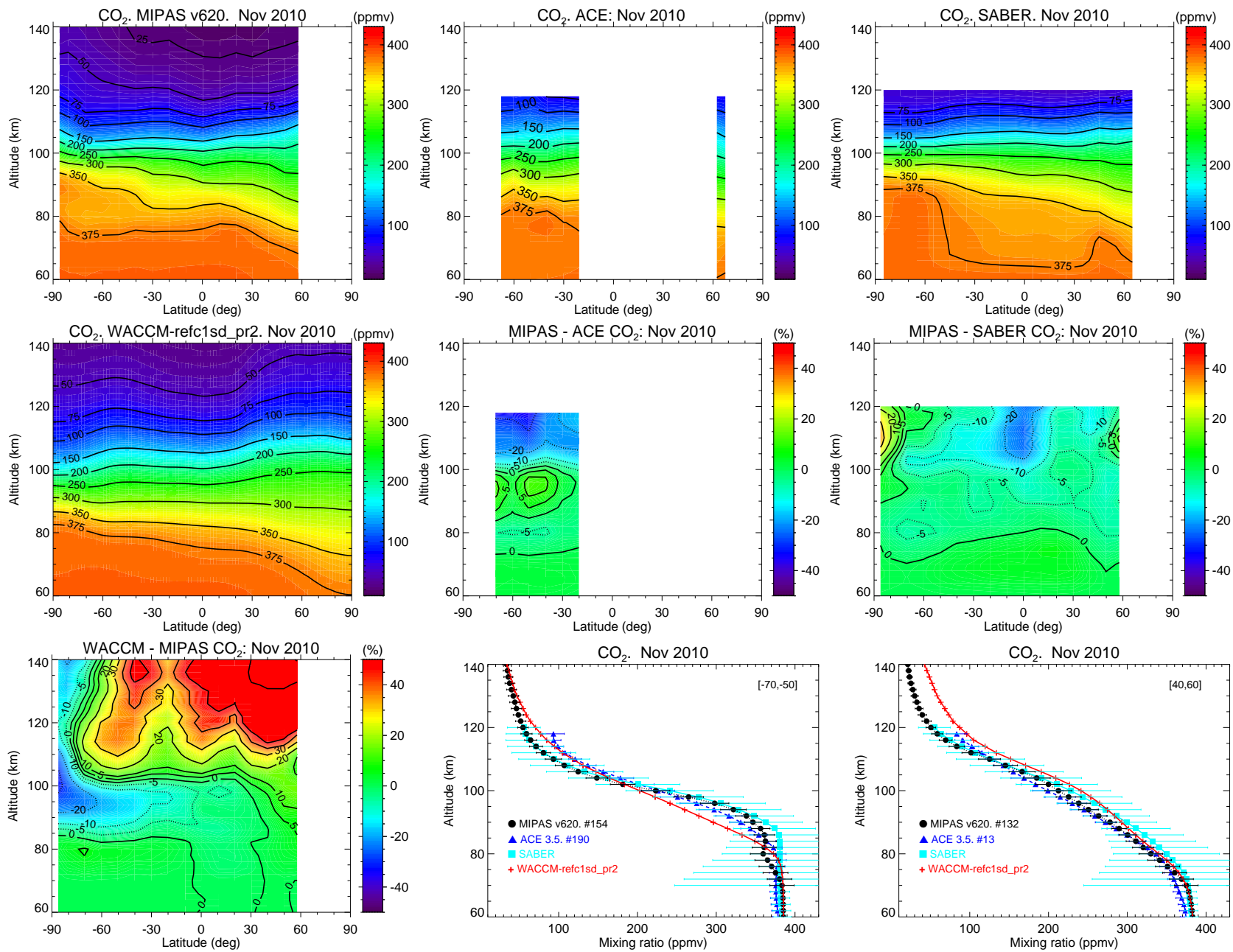


Figure C.11: As Fig. C.1 but for November 2010. Note that the latitude bands in the profiles panels can be different.



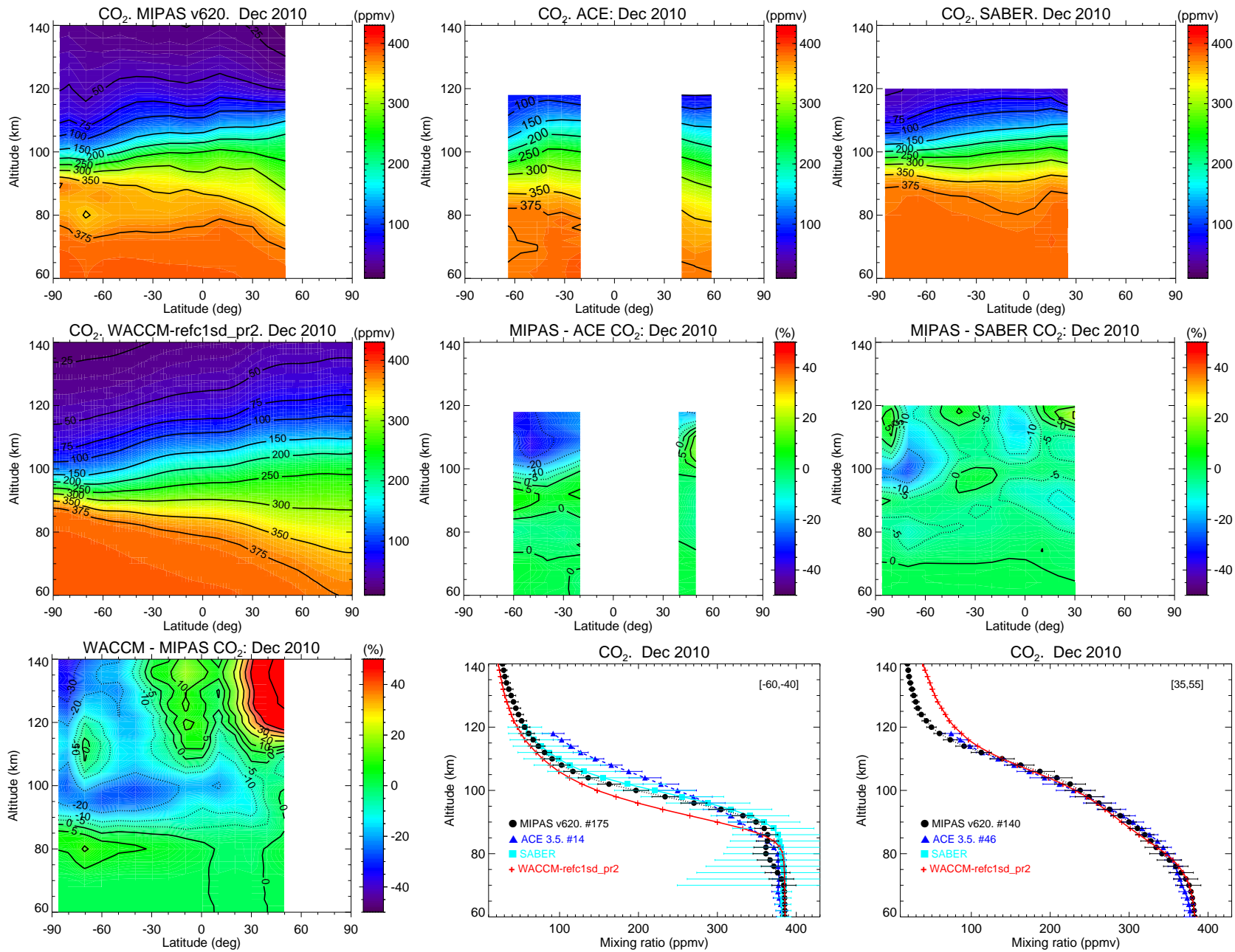


Figure C.12: As Fig. C.1 but for December 2010. Note that the latitude bands in the profiles panels can be different.

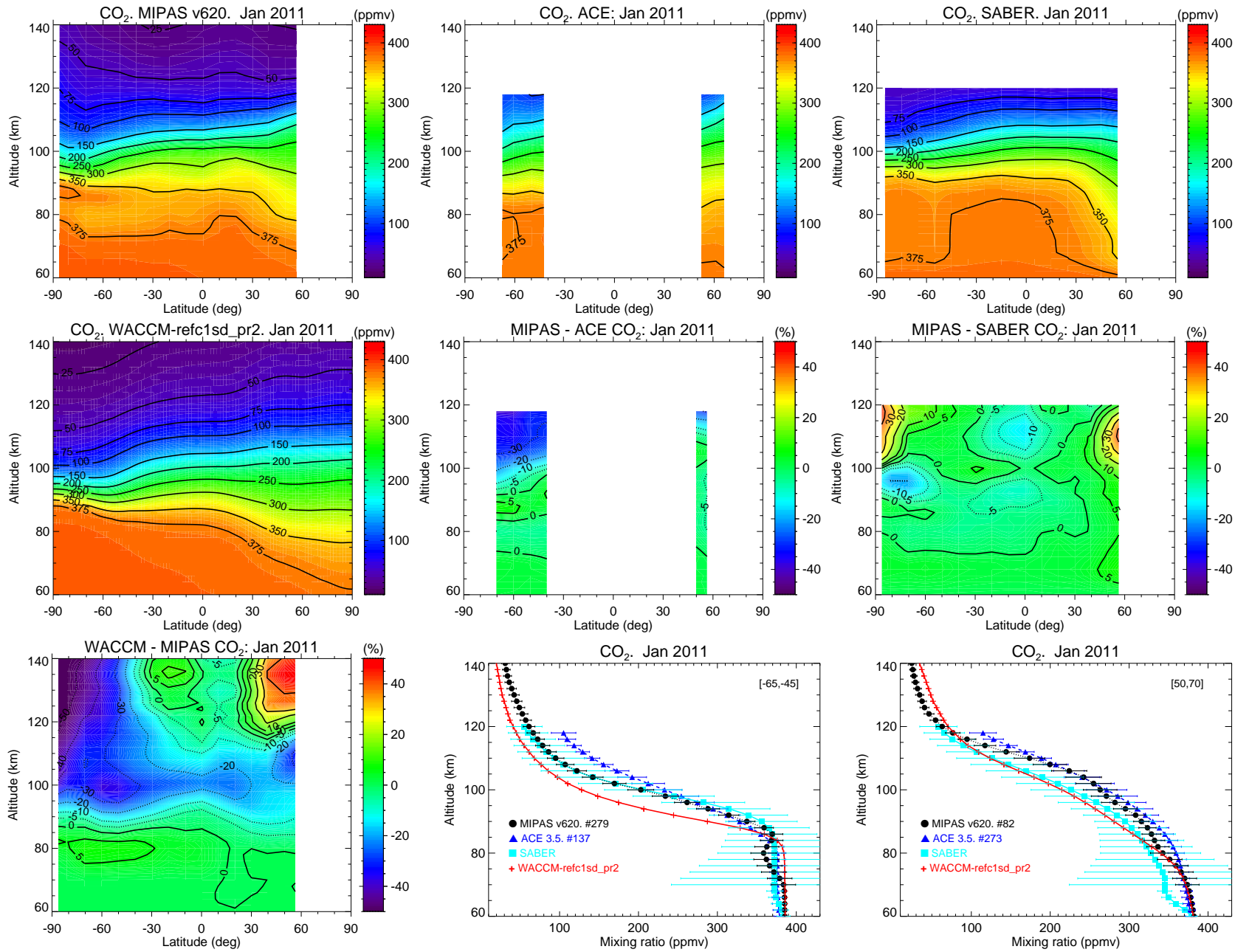


Figure C.13: CO<sub>2</sub> vmr abundances for January 2011. Top row: zonal mean distribution of MIPAS, ACE and SABER, respectively. Middle row: SD-WACCM ( $P_r=2$ ) CO<sub>2</sub> distribution, and MIPAS-ACE and MIPAS-SABER CO<sub>2</sub> relative differences in %. Bottom row: WACCM-MIPAS CO<sub>2</sub> differences, and CO<sub>2</sub> vmr profiles for two latitude bands (as labelled) corresponding roughly to the ACE measurements. Horizontal bars in the measurements are the total errors, dominated by the systematic errors.

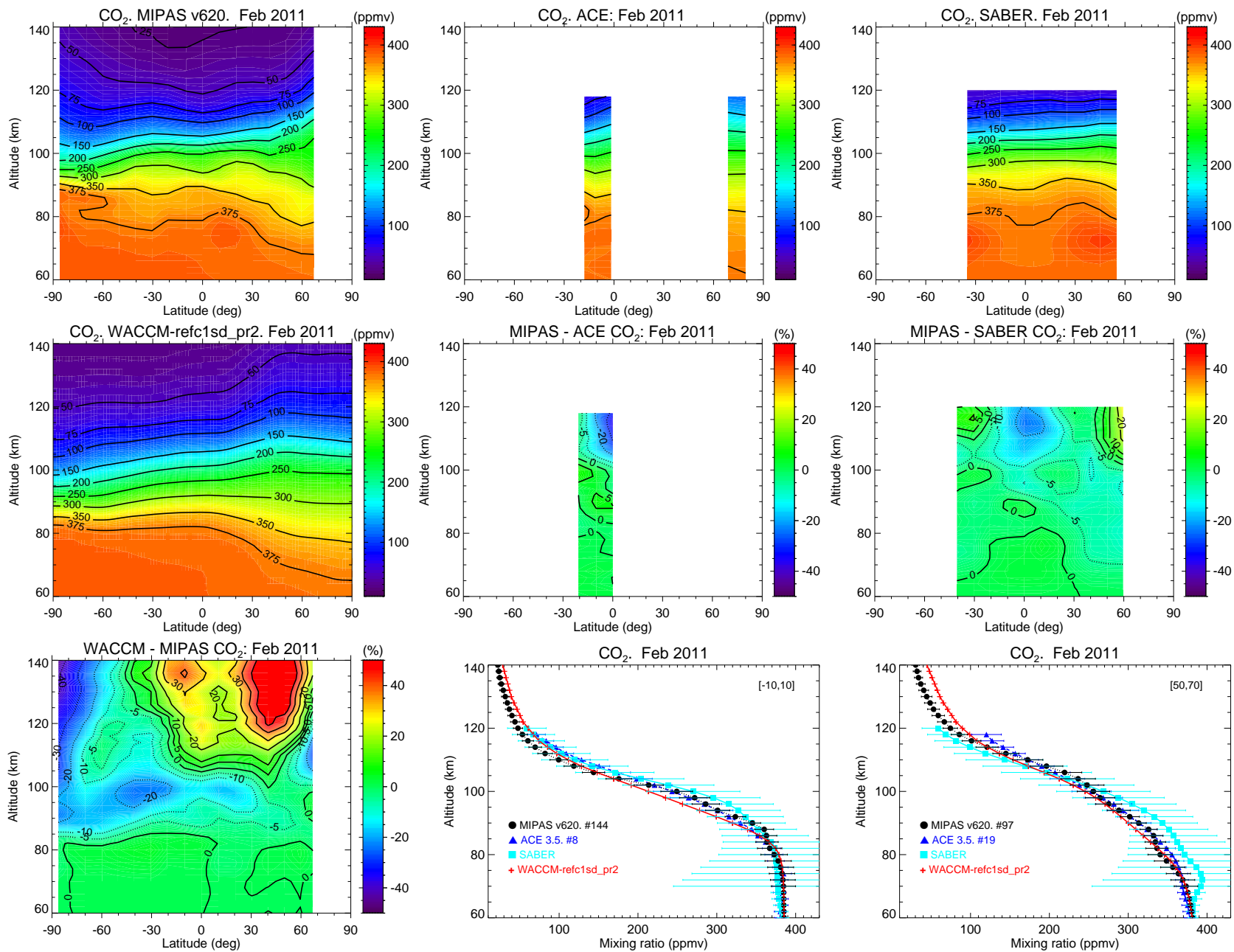


Figure C.14: As Fig. C.1 but for February 2011. Note that the latitude bands in the profiles panels can be different.

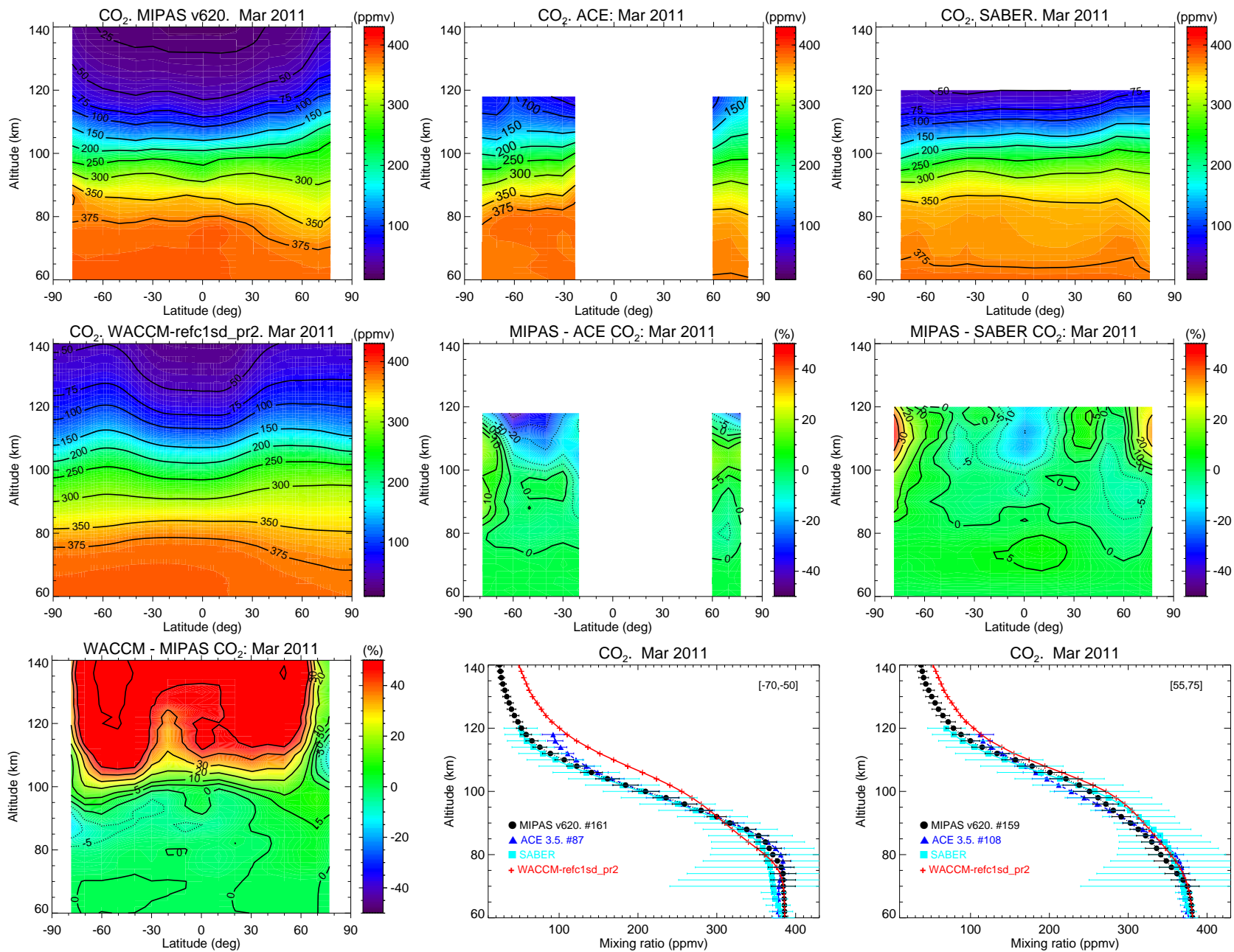


Figure C.15: As Fig. C.1 but for March 2011. Note that the latitude bands in the profiles panels can be different.



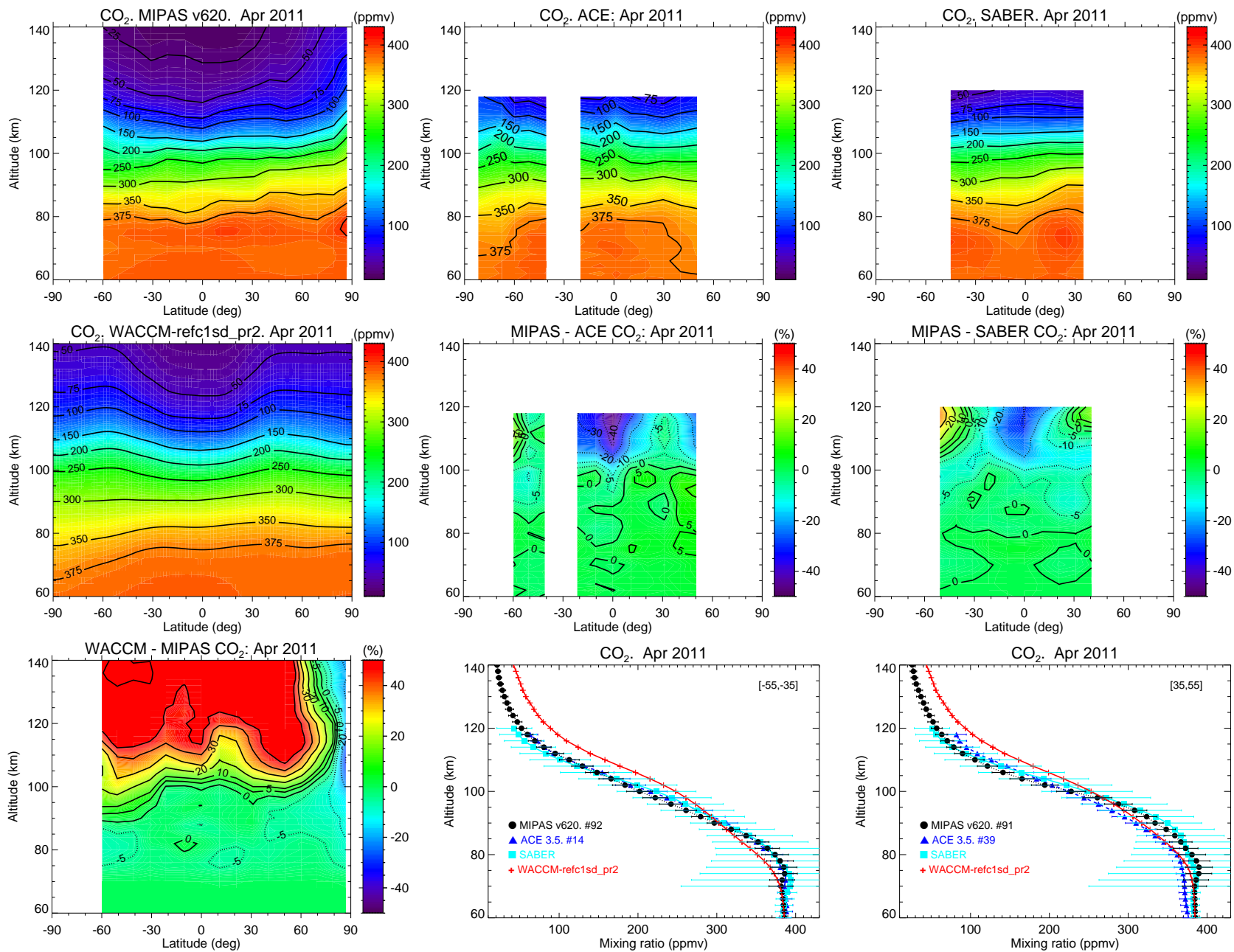


Figure C.16: As Fig. C.1 but for April 2011. Note that the latitude bands in the profiles panels can be different.

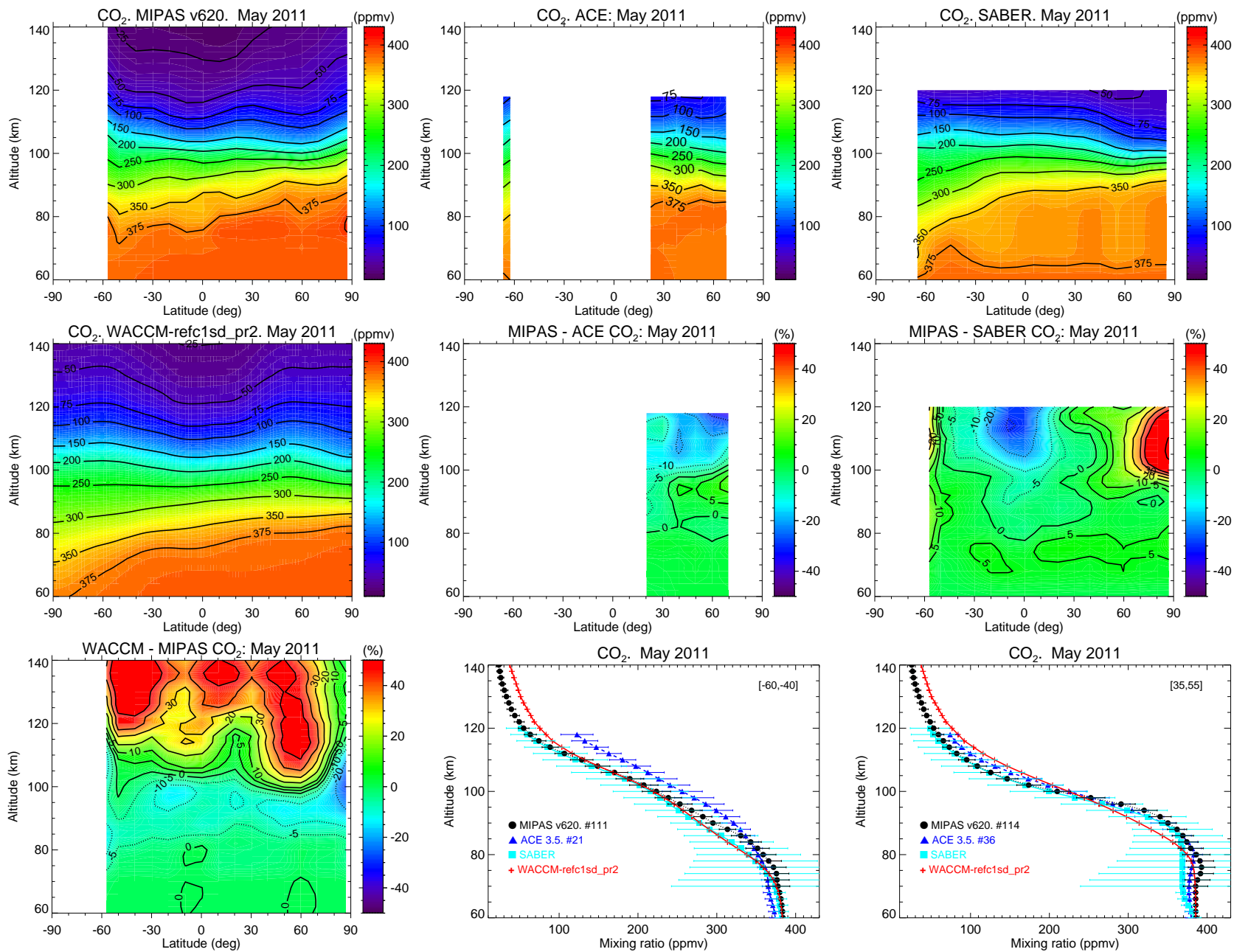


Figure C.17: As Fig. C.1 but for May 2011. Note that the latitude bands in the profiles panels can be different.

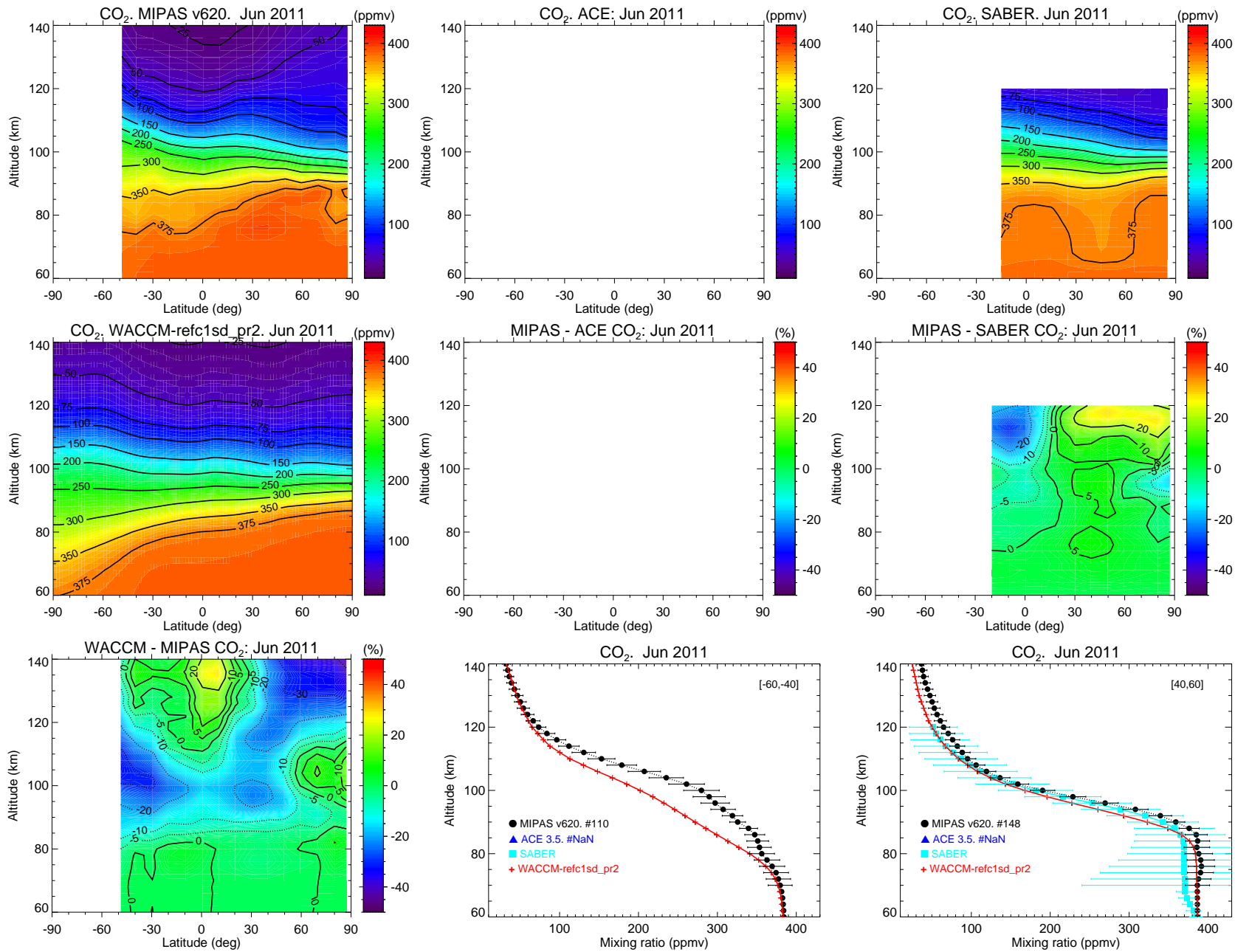


Figure C.18: As Fig. C.1 but for June 2011. Note that the latitude bands in the profiles panels can be different.

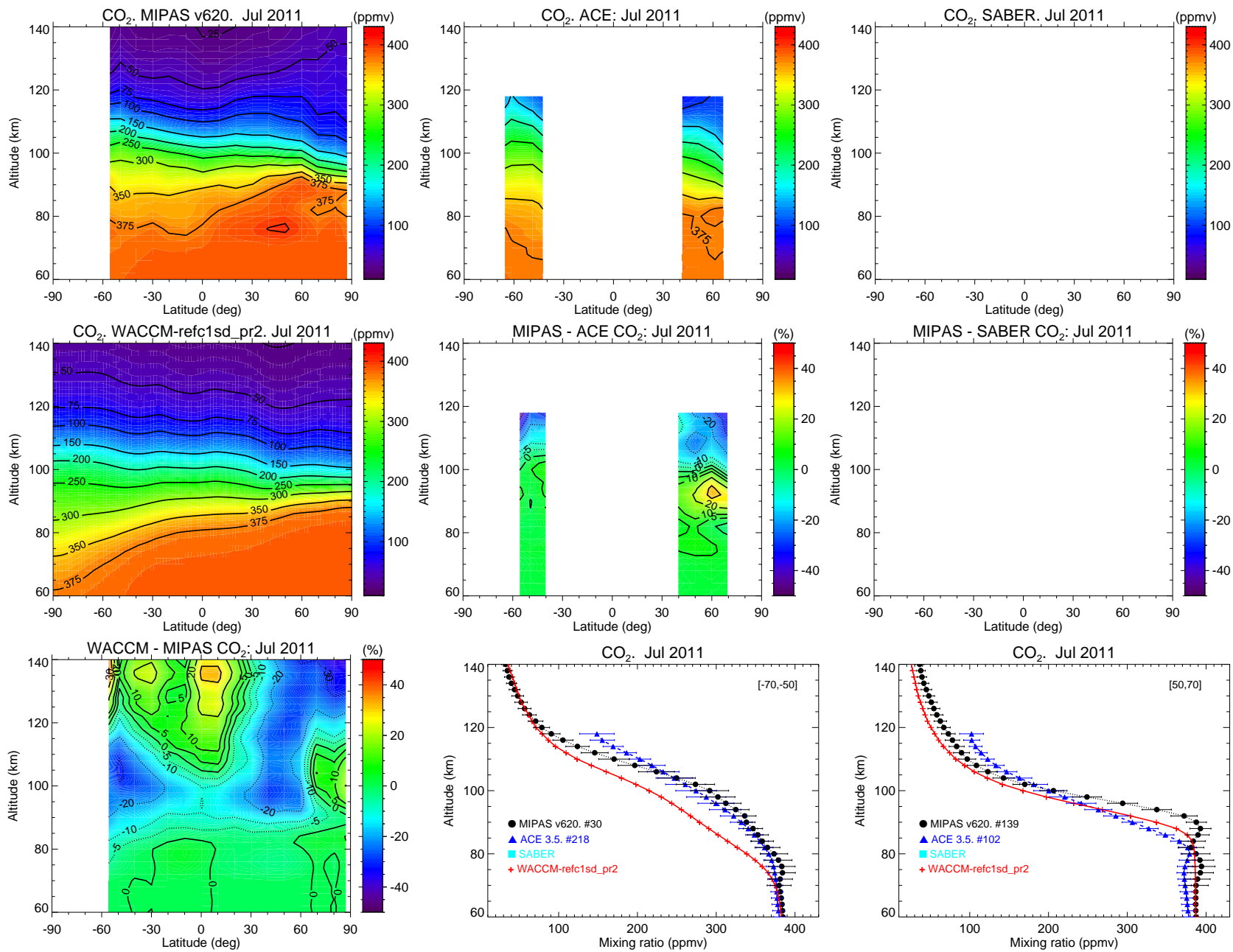


Figure C.19: As Fig. C.1 but for July 2011. Note that the latitude bands in the profiles panels can be different.



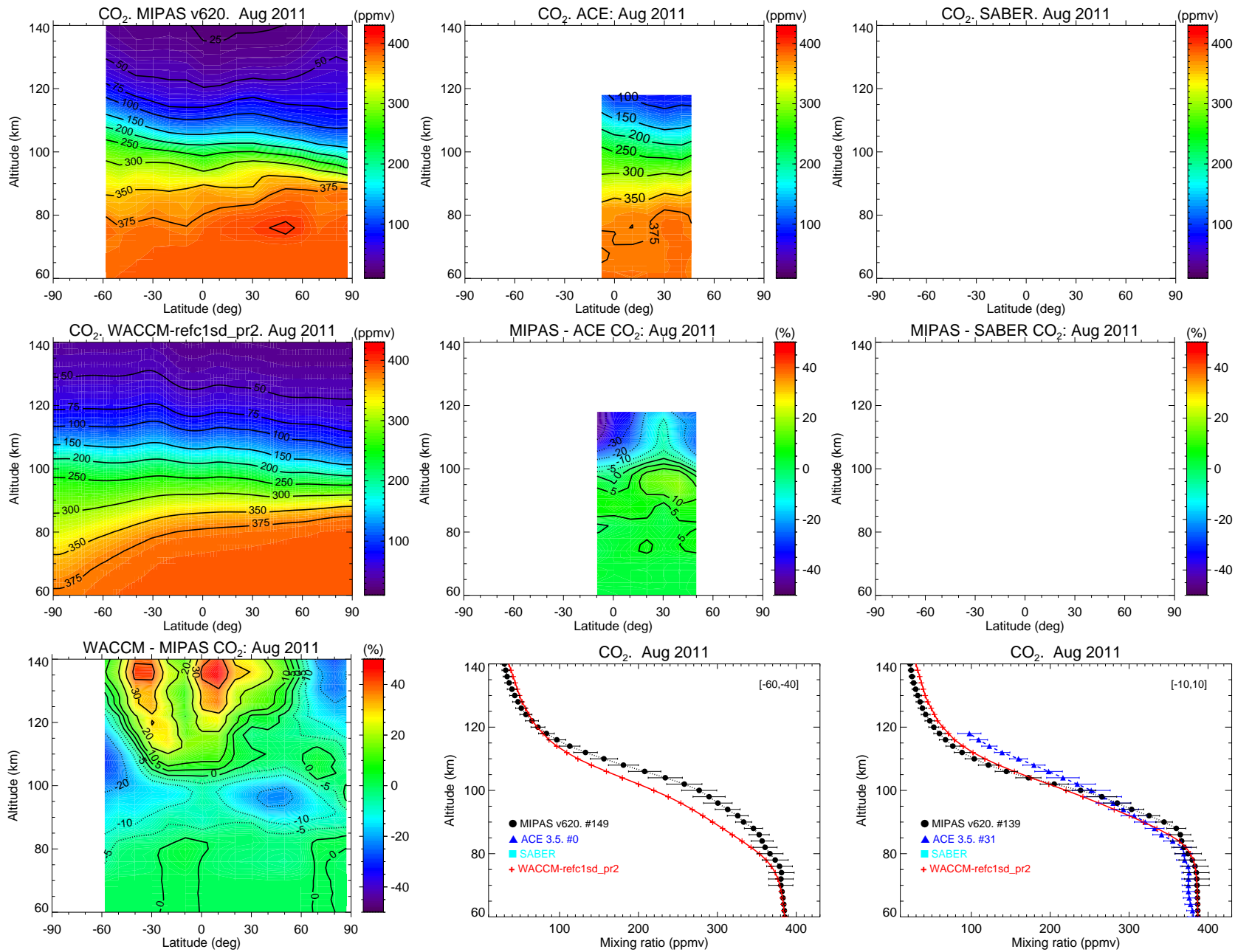


Figure C.20: As Fig. C.1 but for August 2011. Note that the latitude bands in the profiles panels can be different.

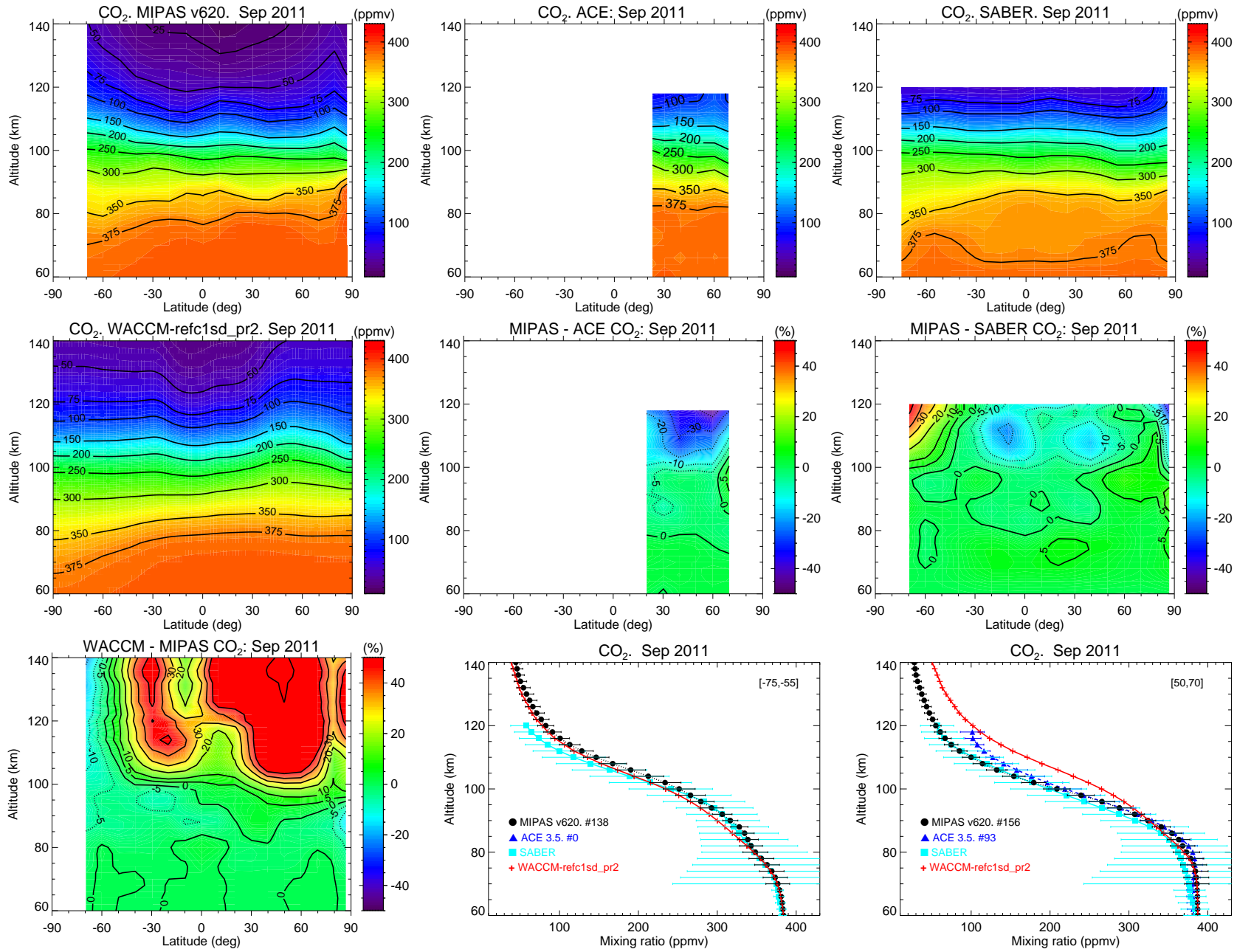


Figure C.21: As Fig. C.1 but for September 2011. Note that the latitude bands in the profiles panels can be different.

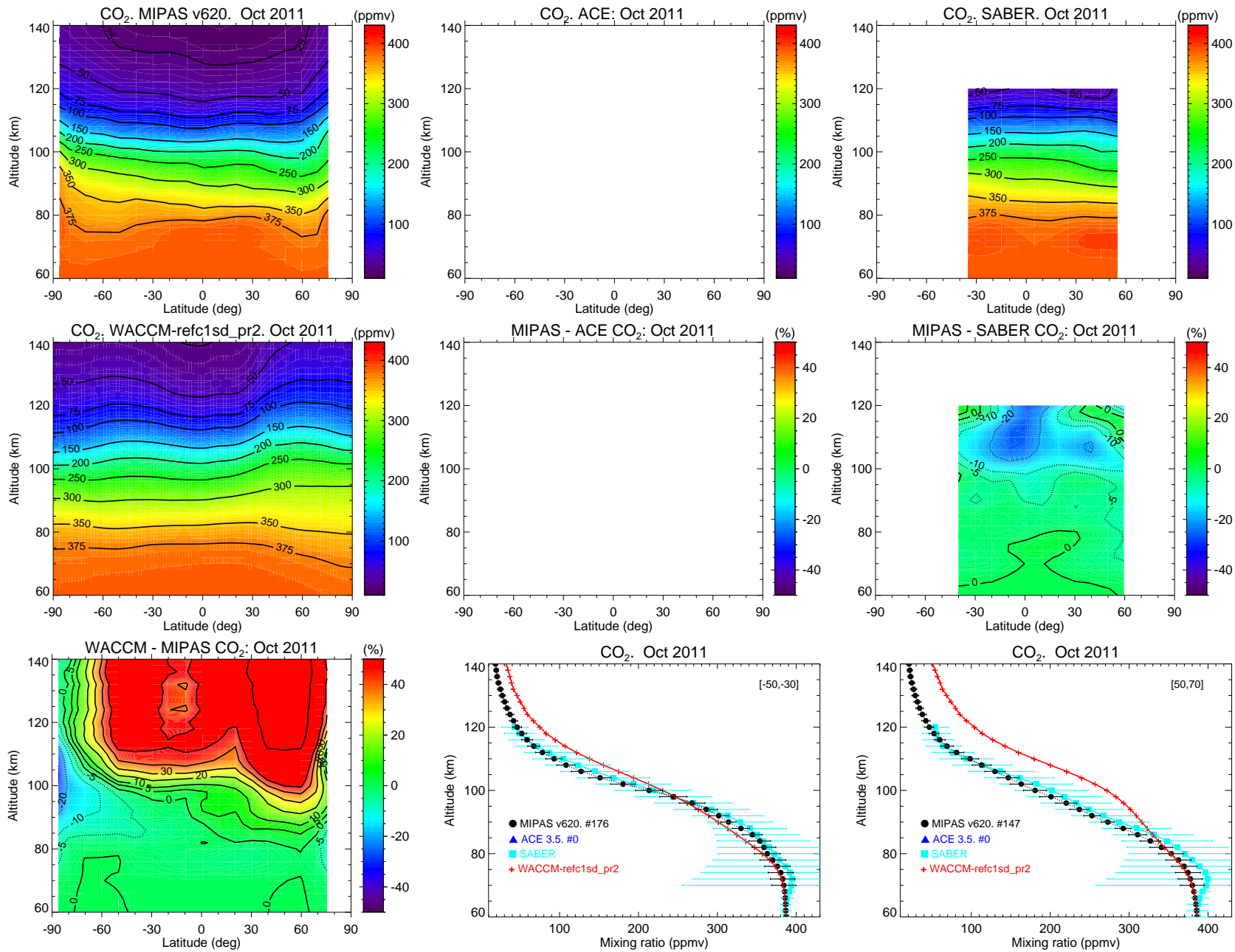


Figure C.22: As Fig. C.1 but for October 2011. Note that the latitude bands in the profiles panels can be different.

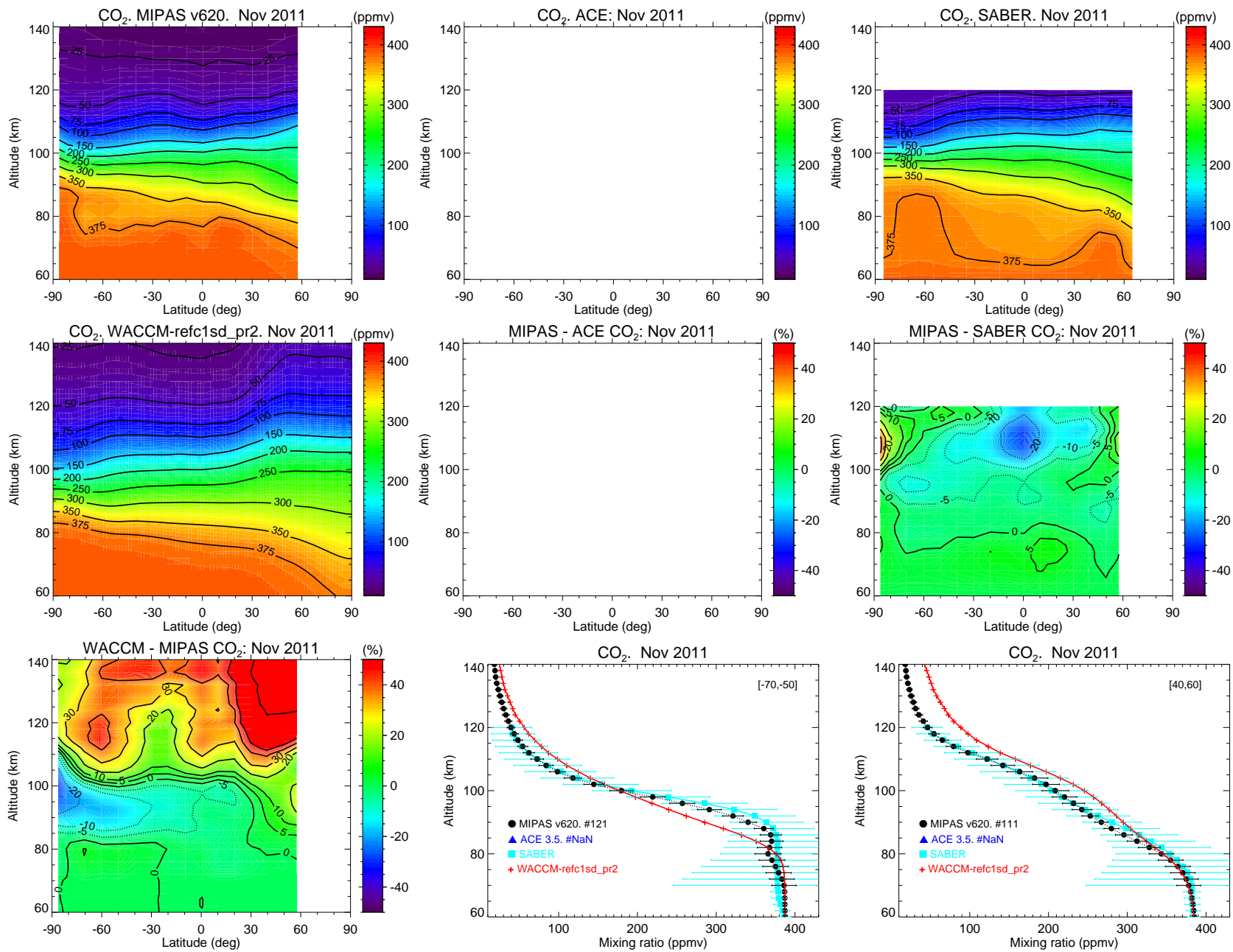


Figure C.23: As Fig. C.1 but for November 2011. Note that the latitude bands in the profiles panels can be different.



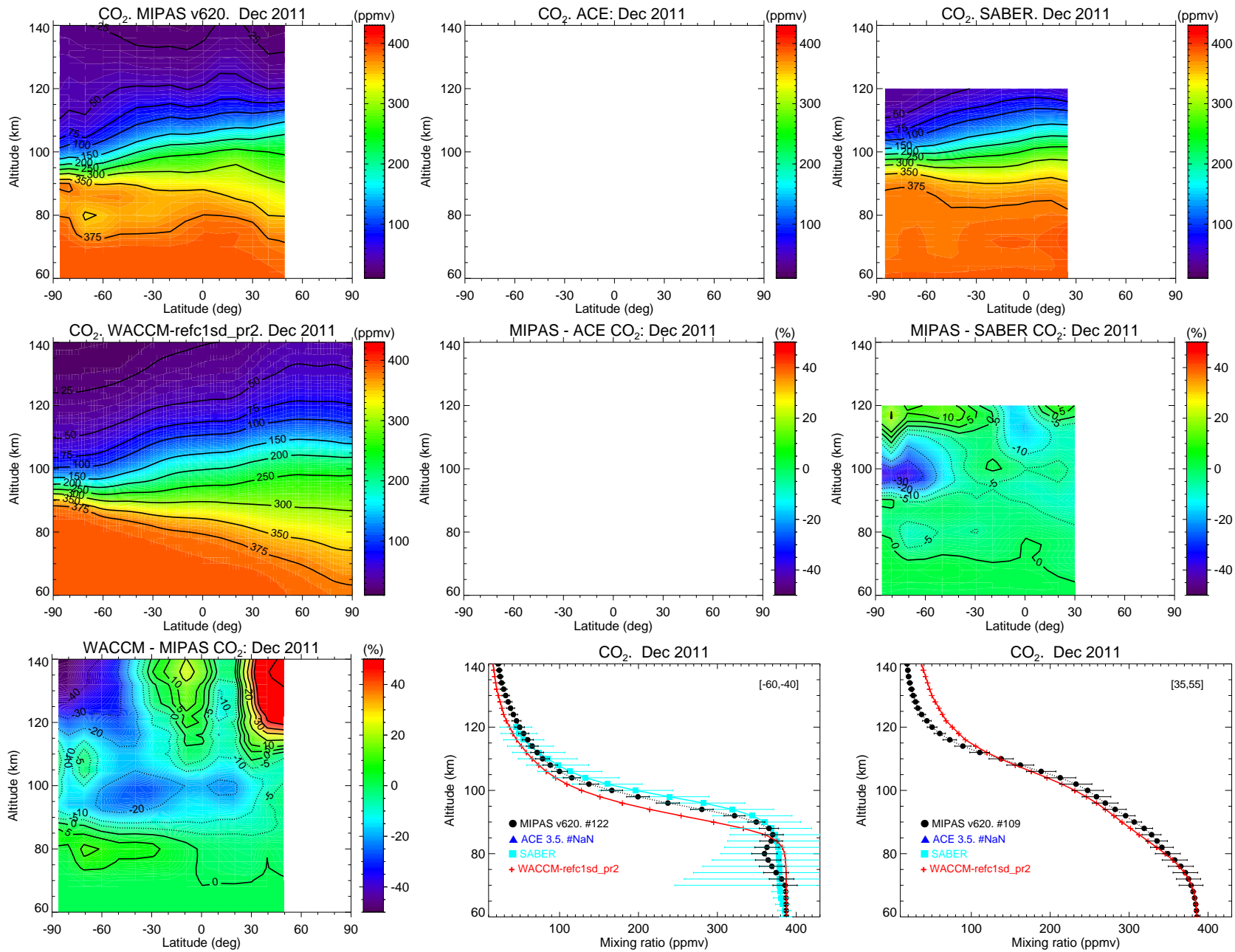


Figure C.24: As Fig. C.1 but for December 2011. Note that the latitude bands in the profiles panels can be different.



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